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BY

ALEXANDER FINDLAY

M.A., D.Sc., F.I.C.

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF WALES
AND DIRECTOR OF THE EDWARD DAVIES CHEMICAL LABORATORIES
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TO

MY WIFE

PREFACE

WHEN the writer was invited to deliver the Thomson Lectures before the United Free Church College, Aberdeen, at the end of the year 1915, he felt that, as a teacher of chemistry, he could attempt no higher task than that of giving to his hearers, who made no claim to chemical knowledge, some account of what the science of chemistry, both in its general principles and in its industrial applications, has accomplished for the material well-being and uplifting of mankind; and the lectures which were then delivered form the basis of the present work.

The reasons which prompted the choice of subject are, of course, not far to seek. The crisis through which this and other European countries are now passing, has brought home to us how greatly we, as a nation, have hitherto failed to recognise the intimate and vital dependence of our social and national prosperity on a knowledge and appreciation of the facts and principles of science, and not least of chemistry, and on their application in industry. All the industries of the country on which not only the comfort but even the life of the people depend—the great manufacturing industries and agriculture, the greatest industry of all—claim tribute of chemistry. And yet we, as a nation, have done much less than the responsibilities of our civilisation demanded, to promote and encourage the development

of chemical knowledge; we have even, indeed, largely failed to avail ourselves of that tribute which science is so willing to pay. To the work of laying the foundation of pure science, on which the superstructure of successful industrial achievement must be raised, British chemists have, according to the measure of their numbers, contributed an honourable share; but the people as a whole, being ignorant of science, have mistrusted and looked askance at those who alone could enlarge the scope of their industries and increase the efficiency of their labours. And so we have witnessed in the past an appalling and needless waste of our national resources, and in too many cases industries have languished and succumbed, or, even when born under conditions of great promise, have remained dwarfed and stunted in growth. In 1862, the German chemist, Hofmann, at that time a Professor of Chemistry in London, could utter the prophecy: "England will, beyond question, at no distant day, become herself the greatest colour-producing country in the world, nay, by the strangest of revolutions, she may, ere long, send her coal-derived blues to indigo-growing India, her tar-distilled crimsons to cochineal-producing Mexico, and her fossil substitutes for quercitron and safflower to China, Japan, and the other countries whence these articles are now derived." But, alas! that prophecy has not yet been fulfilled, and the industry of synthetic dyes, an industry which above all others depends on the fostering and encouragement of chemical research and on the highest scientific efficiency, has found a home elsewhere amid more congenial surroundings.

But there are now welcome signs that the country is

awakening to a sense of past deficiencies, and already the Government has taken a first short step in the direction of encouraging and assisting scientific and industrial research. But if the national effort is really to become effective and to exert a lasting influence, something more is necessary, something which is, perhaps, more difficult of achievement than Governmental aid. The mental outlook and the attitude of the people as a whole towards science must be changed, and the scientific habit, and a spirit of trust in science must be cultivated; and we must also attract in much larger numbers into the ranks of scientific workers, men of equal mental calibre to, and capable of taking the same wide outlook as those who are at present attracted into the higher ranks of the legal profession or into the Civil Services. Science stands for efficiency *in all the activities of life*, and the neglect of science spells waste and industrial decay. It is for the country to choose the path which it will follow, but in making their choice let the people bear in mind the words spoken by the King when Prince of Wales: "Does not experience warn us that the rule of thumb is dead, and the rule of science has taken its place; that to-day we cannot be satisfied with the crude methods which were sufficient for our forefathers, and that those great industries which do not keep abreast of the advance of science must surely and rapidly decline?"

But we must learn to appreciate science not merely on account of its utilitarian value as a means of increasing wealth and material prosperity. From the material point of view, doubtless, "science is the knowledge most worth," and in the case of most people, perhaps, interest in science

centres round its industrial or economic utility. *Nisi utile est quod facias, stulta est gloria* ("All useless science is an empty boast") is a sentiment which will find a wide if not an universal acceptance, but we must beware of interpreting the usefulness of science in too narrow a spirit. The study of science possesses a cultural value which is quite independent of the utility of its applications; and as an instrument of culture, as a means of coming into closer relations with Nature and the Infinite, science claims a fuller and more widespread recognition.

At a time of awakening interest in science, the author hopes that the present attempt to give a readily intelligible account of some of the more important general principles and theories of chemical science and of their applications, may afford to the general reader some idea of the world's indebtedness to the chemist, and may also stimulate the interest of, at least, the younger students of chemical science by presenting to them a picture of that land into a fuller possession of which they one day hope to enter.

My thanks are due to the publishers, Messrs. Longmans, Green & Co., for permission to use Figures 1, 2, 9, and 10, taken from works published by them; and I desire, also, to express my indebtedness to my wife for her assistance not only in preparing the manuscript for publication, but also in reading the proof-sheets.

A. F

Y Glyn,
Llanfarian,
Nr. Aberystwyth.
March, 1916.

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CHAPTER I

INTRODUCTION

CHEMISTRY is a branch of science which deals with matter; with the material universe which is revealed to us by our senses. It studies the different kinds of substances found in the world, whether in the living animal and vegetable organisms, or in the non-living mineral matter of the universe. Chemistry investigates the composition of these substances, the methods of their preparation and their behaviour not only in relation to what are called physical forces but also in relation to other substances; and it endeavours to "manipulate" the different substances so as to obtain from them new materials, either useful or ornamental. Through a knowledge of chemistry one may learn how to prepare, artificially, substances which are normally the products of the vital activity of animal and vegetable organisms, or how to prepare substitutes for these naturally occurring substances. Chemistry, further, occupies itself with the question of how things already manufactured, can be manufactured more economically, or be replaced by more suitable materials; and it helps us to understand how the natural and, it may be, irreplaceable resources of the world, can be economised. On the

science of chemistry, indeed, more than on any other branch of organised knowledge, depend the material well-being and comfort of man.

But the end and aim of chemistry is not merely material. Chemistry offers its contribution also to the deeper interests of the human mind. Occupied as he is with the study of material substances and of the marvellous transformations which he is able to bring about in them, the thinking chemist is forced to look below the surface of things and to seek an answer to the fundamental questions relating to the ultimate constitution and structure of matter, and to the forces which govern the changes and transformations which he observes in his laboratory, or which are wrought out in the larger laboratory of Nature. The study, not merely of the products but also of the principles and laws underlying the processes of chemical change, forms the work of the modern chemist. In its wider sweep, chemistry ignores the conventional and artificial frontiers which mark it off from the other branches of science, more especially physics; and in the last quarter of a century there has been no more fruitful region of experimental and speculative activity than that common territory where the sciences of chemistry and physics overlap.

In attempting a brief and necessarily incomplete survey of chemistry in the service of man, I shall endeavour not merely to recount some of the manifold ways in which chemistry has revolutionised life and has contributed, on the material side, to a civilised existence; but I shall try, also, to indicate, if I cannot do more, some of the principles which underlie chemical change, and some part of the

contribution which chemistry has made to our knowledge of the constitution of matter.

I say here constitution, not nature, of matter. The question of what matter, in its ultimate analysis, may be, whether it consists, as some suggest, of "empty cracks in a stagnant sea of ether," or whether it is, as others suppose, "a persistent strain-form flitting through an universal sea of ether," cannot be discussed here. The *explanation* of matter, that is, the description of matter in terms of something simpler, something more fundamental, lies outside the domain of the chemist. We must be content to accept matter as itself a fundamental reality, as itself an ultimate, beyond which chemistry, at least, does not go.

The question of the constitution of matter is one which has occupied the minds of thinking and reasoning men from the earliest beginnings of philosophic enquiry, more especially as developed among the ancient Greeks. Many and varied were the views which were held, and although the study of these will always prove interesting, it must be borne in mind that the considerations which governed the speculations of many of the ancient philosophers were quite different from those by which the modern scientist feels himself bound. To many of the Greek philosophers, the fact that our eyes make things manifest to us, was no proof that those things exist. By them, intuition, a very valuable gift indeed, and reason were made the all-sufficient grounds of knowledge; and they sought to explain the universe merely by the exercise of a vigorous imagination and a rigorous logic. One cannot therefore wonder that they sometimes lost touch with reality. As has been said: "The intellectual vigour of the philosophers of

antiquity, indeed, was capable of the grandest and most comprehensive views of nature, and often conducted them to the most sublime truths, but in attempting perpetually to soar above the vulgar paths of observation and experience, they speedily became confounded in the mists of error and conceit."

To two only of those ancient views special reference need be made on account of the important part which they played in the evolution of the science of chemistry.

In the philosophy of Aristotle, based on that of Empedocles, we find the conception of one primordial matter which acted as the carrier of certain essential qualities which were taken to be hotness, coldness, wetness, dryness. The elements were regarded not as material things but rather as the combinations of these qualities; and by the union of these in different proportions the different substances were formed.

This conception of the constitution of matter dominated science until the time of Robert Boyle in the seventeenth century; and the idea of the existence of four "elements" (fire, air, earth, water) lingers on, in popular thought, even to the present day. Moreover, so long as the view was held that matter has no reality in itself, but is merely the carrier or embodiment of certain qualities, it is clear that the conversion of one form of matter into another by altering the proportions of the elemental qualities, would appear to be quite feasible; and the aim of the ancient and mediæval alchemists to effect such a transmutation (to wit, a transmutation of the base metals into gold), would seem to be neither hopeless nor absurd.

Fruitless as their efforts in this direction proved, the

alchemists, like the Arabian Geber, the Spaniard Raymund Lully, the German Albertus Magnus, and the English Roger Bacon, added much of the highest value to our knowledge of substances; and some of the materials which they were the first to obtain, like *aqua fortis* or nitric acid, and oil of vitriol or sulphuric acid, are among the most important in the whole of modern chemistry. Wrapping itself up in a cloak of mystery and making pretence of a knowledge which it did not possess, alchemy, doubtless, in many cases, exercised a baneful influence by its appeal to the cupidity and baser passions of men, but it acquired at last a nobler aim and ideal under the influence of Paracelsus, in the sixteenth century. Not the curing of "diseased" metals, as the Arabians called the base metals, but, as the handmaid of medicine, the curing of diseased men, was the true avocation of alchemy; and the study and preparation of drugs became the main object of the chemist. And it is of interest, in this connection, to note that in our older Universities, the predecessors of the present professors of chemistry were professors of medicine; and the makers and sellers of drugs, our pharmacists and apothecaries, are those to whom in the common and legal language of the present day we apply the name of chemist.

Powerful as was the influence exerted by the philosophy of Aristotle, there arose, in time, men who refused to accept the doctrine of the four elements; and the overthrow of this philosophy was completed in the seventeenth century by Robert Boyle, of whom it has been said that "he was the father of chemistry and the uncle of the Earl of Cork."

Pure substances, as Boyle pointed out, can be divided

into two classes. In the one class are those which have, so far, resisted all attempts to decompose them, or to break them down into substances simpler than themselves. These substances, according to Boyle, are the true *elements*, and this definition of an element is still retained. The definition, it should be noted, does not postulate the impossibility of decomposition, but insists merely on the fact that the possibility, if it exists, has not so far been realized.

In the second class of pure substances are placed those which, by one means or another, can be resolved into simpler substances. These more complex substances are called *compounds*. Thus, for example, if we heat in a glass tube the red substance known as red precipitate or oxide of mercury, we find that a gas is given off which has the property that it will cause a glowing splint of wood to re-ignite; and, at the same time, metallic mercury is deposited in shining droplets on the cooler portions of the tube. We have thus decomposed the red substance into metallic mercury and a gaseous substance, to which the name of oxygen has been given. This red substance, therefore, is a compound, a compound of mercury and oxygen.

In spite of most laborious and prolonged efforts, chemists have not succeeded in reducing the number of the elements to less than about eighty. Of these eighty odd elements, a list of which for convenience of future reference we give below, all the substances in the known universe are built up.

List of the Elements.

Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	144·3
Argon	A	39·88	Neon	Ne	20·2
Arsenic	As	74·96	Nickel	Ni	58·68
Barium	Ba	137·37	Niton (radium emanation)	Nt	222·4
Bismuth	Bi	208·0	Nitrogen	N	14·01
Boron	B	11·0	Osmium	Os	190·9
Bromine	Br	79·92	Oxygen	O	16·00
Cadmium	Cd	112·40	Palladium	Pd	106·7
Cæsium	Cs	132·81	Phosphorus	P	31·04
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12·00	Potassium	K	39·10
Cerium	Ce	140·25	Praseodymium	Pr	140·6
Chlorine	Cl	35·46	Radium	Ra	226·4
Chromium	Cr	52·0	Rhodium	Rh	102·9
Cobalt	Co	58·97	Rubidium	Rb	85·45
Columbium	Cb	93·5	Ruthenium	Ru	101·7
Copper	Cu	63·57	Samarium	Sa	150·4
Dysprosium	Dy	162·5	Scandium	Sc	44·1
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Europium	Eu	152·0	Silicon	Si	28·3
Fluorine	F	19·0	Silver	Ag	107·88
Gadolinium	Gd	157·3	Sodium	Na	23·00
Gallium	Ga	69·9	Strontium	Sr	87·63
Germanium	Ge	72·5	Sulphur	S	32·07
Glucinum	Gl	9·1	Tantalum	Ta	181·5
Gold	Au	197·2	Tellurium	Te	127·5
Helium	He	3·99	Terbium	Tb	159·2
Holmium	Ho	163·5	Thallium	Tl	204·0
Hydrogen	H	1·008	Thorium	Th	232·4
Indium	In	114·8	Thulium	Tm	168·5
Iodine	I	126·92	Tin	Sn	119·0
Iridium	Ir	193·1	Titanium	Ti	48·1
Iron	Fe	55·84	Tungsten	W	184·0
Krypton	Kr	82·92	Uranium	U	238·5
Lanthanum	La	139·0	Vanadium	V	51·0
Lead	Pb	207·10	Xenon	Xe	130·2
Lithium	Li	6·94	Ytterbium (Neoytterbium)	Yb	172·0
Lutecium	Lu	174·0	Yttrium	Yt	89·0
Magnesium	Mg	24·32	Zinc	Zn	65·37
Manganese	Mn	54·93	Zirconium	Zr	90·6
Mercury	Hg	200·6			

Only about twenty of the elements occur free or uncombined in nature; and the amounts in which the different elements exist vary very greatly. Of all the elements found in the earth, the seas, and the air, oxygen and silicon are by far the most abundant, as the following analysis shows :—

CHEMICAL COMPOSITION OF THE EARTH.

	Per cent.		Per cent.
Oxygen	49·85	Sodium	2·33
Silicon	26·03	Potassium	2·33
Aluminium	7·28	Magnesium	2·11
Iron	4·12	Hydrogen	0·97
Calcium	3·18	Other elements	1·80

In other words, the two elements, oxygen and silicon, constitute together three-quarters of the whole of terrestrial matter.

Underlying the philosophy of Aristotle was the idea that matter is continuous, that it is capable of infinite sub-division; but with the overthrow of the doctrine of the four elements of Aristotle there was revived another ancient hypothesis which had been put forward by the Greek philosophers Leucippus and Democritus, an hypothesis which has been preserved and expounded for us, with a wealth of poetic imagery, by the Roman poet Lucretius. According to this hypothesis, the ultimate constituents of matter are indivisible particles—the "atoms" or "first beginnings of things"—eternal and immutable, in which, as explained by Aristotle, "the common primitive matter, differing in size and form of its parts, is the principle of them all." By the coming together of these atoms the substances constituting the material world were regarded as being formed; and the diversity of substances was held

to be due to differences in the size and shape of the atoms composing the substances. "Now mark and next in order apprehend of what kind and how widely differing in their forms are the beginnings of things, how varied by manifold diversities of shape. . . . The things which are able to affect the senses pleasantly, consist of smooth and round elements; while all those, on the other hand, which are found to be bitter and harsh, are held in connection by particles that are more hooked, and for this reason are wont to tear open passages into our senses." (Lucretius.)

These views must seem crude to the modern mind, and even Newton, at the end of the seventeenth century, could not greatly refine them. Thus he expressed the view: "It seems probable to me that God, in the beginning, formed matter in solid, massy, hard, impenetrable, moveable particles, of such sizes and figures, and with such other properties, and in such proportion to space, as most conduced to the end for which He formed them; and that those primitive particles, being solids, are incomparably harder than any porous bodies compounded of them; even so very hard as never to wear or break in pieces; no ordinary power being able to divide what God himself made one in the first creation."

The great authority of Newton was a powerful support to the atomic conception of matter, but it was not till the beginning of the nineteenth century that this fundamental hypothesis was developed into a theory by which the observed phenomena and the laws of chemical combination could be *quantitatively* explained or co-ordinated. It was only after this had been done, however, that the general hypothesis of the atomic constitution of matter could

become of any real value in science, and nothing has influenced the progress of chemistry so much as the achievement of this by the Manchester schoolmaster, John Dalton.

To the older philosophers, the atoms or indivisible particles into which matter could be divided, all consisted of the same primordial material, although differing in size and shape. The atoms of Dalton, however, differed in their nature. In the case of any particular element, the definition of which we have already learned, the atoms were assumed to be all exactly alike in their properties, including, of course, their mass; but they differed from the atoms of any other element.

Further, according to Dalton, a compound is formed by the coming together or combination of atoms of different kinds; and since the nature of the compound will necessarily depend on the number and kind of the atoms present, *the composition of the compound must be definite.* This is the first fundamental law of chemistry, the law of constant or definite proportions.

And still further. Since the fundamental assumption of the atomic theory is that atoms are indivisible, that they cannot be broken up into anything smaller, it follows that if one particular element A combines with another element B to form compounds containing different proportions of A and B, the higher proportions of the elements must be *whole* multiples of the lowest proportion. That is to say, we can have the compounds A + B, A + 2B, 2A + B, 2A + 3B, etc., where A and B represent atoms of the elements A and B. Here, then, we have the explanation of the second fundamental law of chemistry, the law of multiple proportions.

JOHN DALTON, 1766-1844.

To face p. 10.

At first Dalton made no distinction between the smallest particle of an element and the smallest particle of a compound. Both were called atoms. But it is clear that this must cause difficulty, because although the atom of an element may be regarded as indivisible, the atom of a compound must still be capable of being split up into smaller particles, namely the atoms of the component elements. A new name was therefore introduced by the Italian chemist, Avogadro, who called the smallest particle of a compound a *molecule;* and a molecule of a compound, therefore, consists of a number of elementary atoms. We have, then, the definition that an atom is the smallest particle of an element which can enter into the composition of a molecule, or which can take part in chemical exchange. It is, so to speak, the smallest coin in chemical currency. A molecule, on the other hand, is the smallest particle of a substance *which can exist in the free state.*

But it does not follow that the atoms and molecules of an element mean the same thing. In some cases they do, and the atoms of such elements as argon and helium, for example, can exist in the free state, by reason of the fact that they possess no power of combination. But in very many cases the free atoms of an element combine together to form aggregates of like atoms, so that the molecule of an element, or the smallest particle of the element capable of free existence, may consist of two or three or even of four atoms combined together.

In the table given on p. 7, we see that opposite each element is a letter or group of letters, by means of which we can represent shortly the particular element. Each of

those *symbols*,[1] as they are called, represents an atom or one atomic proportion of the particular element; and since a compound is regarded as being formed by the combination of atoms, we can conveniently represent the molecule of a compound by writing the symbols of the constituent atoms side by side. Thus, NaCl represents a compound of sodium and chlorine, the molecule of which contains one atom of sodium and one atom of chlorine; CO, similarly, represents a compound of carbon and oxygen; and so on. But, frequently, the molecule of a compound is formed by the combination of elements in more than one atomic proportion, and so we write, for example, H_2O, which is the *formula* (as it is called) for water; a formula which indicates that the molecule of water contains two atoms of hydrogen and one atom of oxygen. The formula NH_3, similarly, which is the formula for ammonia, indicates that the molecule of this compound contains three atoms of hydrogen united with one atom of nitrogen.

The use of these symbols and formulæ is a great convenience and renders much assistance to the chemist in understanding chemical changes; and we shall make use of them to some extent in our future discussions.

To one point more we must refer. According to the

[1] These symbols were introduced early last century by the Swedish chemist Berzelius, who used the initial letter of the Latin name to represent the element. Where the name of more than one element began with the same letter, a second letter was added as a distinguishing mark. By using he Latin names of the elements, the symbols were rendered international; and we can thus understand why, in certain cases, the symbols are not obvious abbreviations of the English name of the element. Thus, we have, Sb = antimony (stibium); Cu = copper (cuprum); Au = gold (aurum); Fe = iron (ferrum); Pb = lead (plumbum); Hg = mercury (hydrargyrum); K = potassium (kalium); Ag = silver (argentum); Na = sodium (natrium); Sn = tin (stannum).

atomic theory of Dalton, the atoms of a particular element are all exactly alike, and different from the atoms of other elements. If the atoms have definite properties, however, they must also have a definite mass or weight. Although shrewd estimates of the absolute weights of atoms have been made, it is clear that we cannot handle these infinitesimally small particles of which many millions are contained in the tiniest piece of matter which can be seen by the eye; we cannot place these atoms on the scale pan of our balance and ascertain their weight. But we can determine the *relative* weights of the atoms, and such determinations constitute one of the greatest achievements of science which followed in the train of Dalton's atomic theory. These relative weights are what are called the *atomic weights* of the elements, and their values are given in the table on p. 7. By the introduction of these atomic weights, a new and extended meaning is given to our formulæ. NaCl then becomes not merely a convenient shorthand symbol for the compound sodium chloride (which is the chemical name for common salt), but it tells us that this compound consists of one atomic proportion or 23 parts by weight of sodium, and one atomic proportion or 35·46 parts by weight of chlorine, the numbers 23 and 35·46 being the relative weights of the sodium and the chlorine atom respectively.

One of the greatest of scientists, Lord Kelvin, said: "I often say that if you can measure that of which you speak, and can express it by a number, you know something of your subject; but if you cannot measure it, your knowledge is meagre and unsatisfactory." And it is because Dalton's theory is a quantitative theory, or

capable of quantitative expression, that it was possible for the hypothesis of the discontinuous or atomic constitution of matter to become the foundation stone of all modern physical science; and it is by the introduction of mathematics and by the quantitative treatment of chemical phenomena, that modern chemistry is mainly distinguished from the chemistry of fifty years ago.

CHAPTER II

COMBUSTION AND THE PRODUCTION OF FIRE

ONE of the most typical, most familiar, and most important cases of chemical action is that which is observed in the process of combustion or the burning of substances in air. The manner in which the first visible combustion, or fire, was brought about on the earth, whether by some lightning flash, or by the sparks struck from the flints of primitive man; by the rubbing together of dried wood, or by the self-heating of combustible material, will doubtless always remain unknown. But in whatever way fire was first produced, its importance and value were early recognised, as we can understand from the sanctity with which all primitive peoples have endowed the hearth; from the Promethean legend of a boon stolen from, not granted by the gods; as well as from the later belief of the followers of Zoroaster, that fire is the special abode of divinity.

And even in modern times, although the feeling of reverence or of awe is no longer inspired by a process which can be explained in terms of chemical action, and can be produced at will by the striking of a match, we are not likely to underrate the importance of combustion when we remember that our present-day civilisation, in all its manifold forms of expression, in manufactures,

in railway and steamship transport, in artificial illumination, etc., is based on a process of combustion.

What then is the explanation of this process of combustion? Not so very long ago, the view was held that the property of combustibility was due to the presence in the combustible substance, of a fiery principle, phlogiston; and that when a substance burns, the phlogiston escapes, leaving behind the ash, or calx, as it was called in the case of a metal. Charcoal, which burns leaving practically no ash, was therefore regarded as being almost pure phlogiston. This was the explanation of combustion given, more especially, by Stahl, towards the end of the seventeenth century; and it was not till a hundred years later that the "phlogiston theory" was finally overthrown by the French chemist Lavoisier, who died in 1794, a victim of the guillotine, in the troublous times of the French Revolution.

The long life of such an erroneous theory as that due to Stahl may be attributed to the fact that chemistry was, at that time, still largely a qualitative or descriptive science, and it was considered that form rather than weight was the characteristic property of substances. The balance, of course, was known and used, but its importance was not fully appreciated; so that when it was found that the products of a combustion weigh more than the original combustible substance, the upholders of the phlogiston theory sought to defend their position by identifying phlogiston with the principle of levity. The escape of the principle of levity from the body, left the body heavier.

Much as we may be inclined to smile at such an explanation, we must remember that the phlogiston theory served

usefully its day and generation, and satisfied even the modern requirements of a theory, in that it gave an explanation of combustion which satisfied men's minds at the time, and also inspired a large amount of fruitful investigation. Who can say that even some of our most cherished theories may not be considered by the unthinking a hundred years hence, to be equally worthy of derision? The phlogiston theory, however, long outlived its usefulness, and the tenacity with which it maintained itself is an instructive illustration of the difficulty which most minds have of freeing themselves from the authority of a long-held theory; and it conveys a lesson, which is not unnecessary even at the present day, that a theory from being a helpful guide may readily become an oppressive tyrant. As Liebig wrote many years ago, after having himself been a victim of the misfortune to which he refers: "No greater misfortune could befall a chemist than that of being unable to shake himself free from the power of preconceived ideas, and, yielding to the bias of his mind, of seeking to account for all phenomena which do not fit in with these ideas by explanations which have no basis in experiment."

But the irresistible force of facts was gradually increasing, and after the discovery of the gas oxygen by Priestley and by Scheele, in the year 1774, Lavoisier was able to put forward a new interpretation of the process of combustion of substances in air; and with that interpretation, modern chemistry was born.

Air is, essentially, a mixture (not a compound), of the two invisible gases, oxygen and nitrogen.[1] The former of

[1] Air contains also, quite normally, small quantities of carbon dioxide (carbonic acid gas) and water vapour, both of which play an important part

these, constituting about one-fifth of the air by volume, not only allows combustion to take place, but promotes it to such an extent that a glowing splint of wood, when immersed in the gas, bursts into flame, and the substance phosphorus burns with dazzling brilliancy. Oxygen is very "active," and combines with practically every other element, the process of combination being known as *oxidation*. Nitrogen is, however, an inert gas, and even the most brightly burning phosphorus is extinguished when introduced into it. The explanation of combustion is thus not far to seek, and is to be found, as Lavoisier proved by the actual weighing of the substances, in the chemical combination of the burning substance with the oxygen of the air.[1] The process of combustion, in other words, is a chemical reaction, a process of oxidation of the combustible substance by the oxygen of the air, which is accompanied by the emission of heat and light; but a flame is formed only when the burning substance is a gas at the temperature of the combustion. The nitrogen of the air takes no part in the process, but acts merely as a diluent which moderates the vigour of the combustion.

But if combustion in air is a chemical reaction between

in the economy of nature; as well also as the rare gases argon, helium, neon, krypton, and xenon.

[1] It may, perhaps, also be remarked in passing, that it was Lavoisier, who, owing to the constant use which he made of the balance and the importance which he attached to its indications, established the fundamental law of material science, the *law of the conservation of matter*, which states that in no chemical action is matter either created or destroyed; the sum of the masses of the reacting substances is equal to the sum of the masses of the products formed. The matter can be changed in form; it cannot be altered in quantity. All later experimental investigation, even the most recent, carried out with all the care and refinement of accuracy of which the modern balance is capable, has served only to confirm this law discovered by Lavoisier.

the combustible substance and the oxygen of the air, why does the former not take fire when exposed to the air? We may allow the coal gas to escape from the burner, or a candle or piece of wood or coal may be left exposed to the air, or even to pure oxygen, without any apparent change taking place; and in order that they shall exhibit the phenomenon of combustion, that is, in order that they shall undergo the process of oxidation, or combination with oxygen, with production of heat and light, it is necessary to heat the materials up to a certain temperature, called the *ignition point* of the substance. Combustion then goes on of itself. The explanation of this fact is that the velocity or vigour of every chemical change is increased by elevation of the temperature. At the ordinary temperature, the oxidation of the candle or the coal takes place so slowly that no change is apparent even over long periods of time. If, however, the temperature of the combustible material is raised, the rate at which it reacts with the oxygen of the air rapidly increases, and consequently the production of heat which accompanies the reaction also rapidly increases, until, at a certain point, the ignition point, the reaction takes place with such rapidity that the heat which is produced by the process of oxidation is sufficient to raise the substances to incandescence and also to maintain the burning substance at a temperature above the ignition point. The process of combustion is thus enabled to proceed continuously.

On the other hand, if the burning substance is cooled sufficiently, the temperature is lowered to below the ignition point, and so the combustion ceases. A simple experiment which can be carried out by any one will

serve to demonstrate this important truth. If we hold a piece of metal wire gauze at a distance of half an inch or an inch above a burner from which coal gas is issuing, and if we then apply a light to the gas *above the gauze*, we shall find that the flame of burning gas is arrested by the gauze and does not pass through to the burner (Fig. 1); for the wire gauze conducts the heat of the flame away so rapidly that the temperature is lowered to below the ignition point of the gas. Only after the gauze has become quite hot does the gas below the gauze become ignited. Similarly,

FIG. 1.

if the gauze is brought down on a flame of burning gas, the flame is extinguished at the gauze. The gas itself, however, passes through, as can be shown by bringing a light to the upper surface of the gauze, when the gas will take fire.

The cooling power of wire gauze received, early last century, an application of the highest importance in the miner's safety lamp invented by Sir Humphry Davy. This lamp has undergone a striking change and marked improvement since the time of its first invention, and the modern safety lamp (Fig. 2) shows little sign of the means whereby safety is secured. But on careful examination it is seen that all the holes through which air can pass to the

flame, or the hot air and products of combustion can pass out, are protected by fine wire gauze. Although, therefore, the combustible gas, the "fire-damp," can pass through this gauze and can burn inside the lamp, the flame cannot pass through the gauze and be communicated to the explosive mixture of fire-damp and air in the mine.

Warning of the presence of the dangerous fire-damp is given to the miner through the luminous flame of the lamp

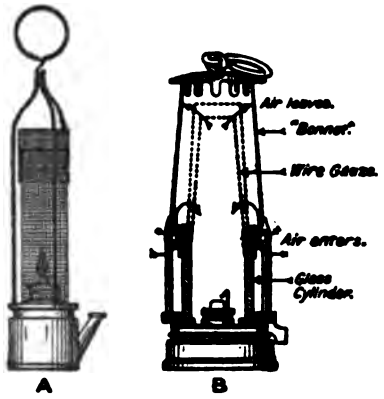


FIG. 2.—MINER'S SAFETY LAMP.

In the old form of lamp, the flame was surrounded by a closed cylinder of wire gauze which considerably diminished the light emitted by the lamp; but in the modern type, a cylinder of glass is inserted, whereby the efficiency of the lamp is greatly increased.

becoming crowned by a "cap" of pale blue flame. The greater the amount of fire-damp the larger is the cap.

The process of combination with oxygen which, as we have seen, is the essential feature of the combustion process in air, may, however, go on appreciably even at temperatures below the ignition point. Thus, when metallic iron is exposed to moist air, it rusts. This rust is oxide of iron, a compound of iron and oxygen; and the process of rusting is therefore a process of oxidation, a process of

combustion, against which it is necessary to protect, by paint or other means, all iron structures exposed to the air, if we would have them last. This *slow combustion*, as it is termed, can be demonstrated more strikingly with the metal aluminium, which has a greater affinity for oxygen than iron has. When finely divided aluminium is heated in the air, as, for example, when aluminium powder is blown through a flame, it burns with a very bright light; but when exposed to the air at the ordinary temperature, the metal remains apparently unchanged. As a matter of fact it rapidly combines with the oxygen of the air, but the coherent film of oxide which is formed on the surface, protects the metal from further attack, and therefore no change is apparent. But let us now coat the surface of the metal with mercury. By this means a liquid amalgam or alloy of mercury and aluminium is produced, and the formation of a coherent film of aluminium oxide is thereby prevented. The aluminium is consequently no longer protected from the continued action of the oxygen of the air. In this case we observe that the aluminium undergoes oxidation quite rapidly, the oxide forming a moss-like growth on the surface of the metal. The heat which is produced by the oxidation, although quite marked, is dissipated so quickly that the temperature does not rise to the point of incandescence, and so no light is seen.

Processes of slow combustion, or combustion unaccompanied by the emission of light, are going on continually within our bodies, and are the source of the heat by means of which the temperature of the body necessary for health, is maintained. When air is drawn into the lungs, the oxygen passes or diffuses through the thin walls of the

blood vessels, and is absorbed by the blood, whereas carbon dioxide passes from the blood into the air-spaces of the lungs and is expelled in the expired air. The oxygen is carried by the blood to all parts of the body, and oxidises or burns the tissues and assimilated food materials with production of carbon dioxide and water, the former being then conveyed by the blood back to the lungs and so got rid of.

The presence of carbon dioxide in expired air is readily shown by blowing through a tube into clear lime water (a solution of slaked lime in water). The liquid very speedily becomes turbid owing to the separation of insoluble carbonate of lime, formed by the combination of carbon dioxide with the slaked lime. The production of a turbidity with lime water is used as a *test* for, or method of, detecting the presence of carbon dioxide.

In the processes of putrefaction and decay, also, we have examples of slow combustion, in which animal and vegetable material is oxidised by the oxygen of the air, with the co-operation of various micro-organisms; and efficient aeration, as in a rushing and tumbling stream, is an excellent means of purifying water from all kinds of organic and bacterial contamination.

Under favourable conditions, the process of slow combustion may pass into rapid combustion with production of light. For, if the heat which is produced by the combination of the oxygen with the combustible material is prevented from being dissipated, the temperature will go on rising gradually, and as the temperature rises, the vigour of the combustion increases. More and more heat, therefore, is produced in a given time, the temperature

rises more and more rapidly until, finally, it reaches the point at which light is emitted. The slow combustion passes into rapid combustion, and the combustible material takes fire without the application of external heat; in other words, it undergoes *spontaneous combustion*. In this way arise, for example, the so-called "gob" fires, in spaces from which coal has been removed, and where coal-dust and fine coal remain behind; so also may fire break out in coal bunkers and in other confined spaces in which combustible matter, like oily cotton waste, is stored without proper ventilation. Such spontaneous combustion will, of course, take place with special readiness in the case of readily inflammable substances, or substances which have a low ignition point, such as phosphorus. Thus if this substance is dissolved in the liquid known as carbon disulphide, and if the solution is then poured on a sheet of filtering paper, or thin blotting-paper, the carbon disulphide soon evaporates and leaves the phosphorus on the paper in a finely divided state. The oxygen of the air rapidly unites with the phosphorus, and the heat which is thereby developed soon raises the temperature to the ignition point of the phosphorus, and rapid combustion sets in.

Although the most familiar examples of combustion are those which take place in air, the term combustion must not be restricted only to such cases. Combustion, in its widest meaning, is a process of chemical action in which so much heat is generated that the burning substance becomes incandescent and emits light; and such a process may occur even when no air or oxygen is present. Thus, for example, the gas hydrogen will burn not only in air,

with production of the substance water, but it will also burn in the gas chlorine with formation of the compound known as hydrogen chloride or hydrochloric acid gas. And similarly, other cases of combustion are known which do not depend on the presence of oxygen, and are not processes of oxidation.

Even when the combustion is due to the combination of the combustible material with oxygen, to a process of oxidation as we have called it, the oxygen need not be present in the gaseous form, but may be yielded up by some compound containing it. Various well-known substances, such as chlorate of potash and saltpetre (potassium nitrate), can act as suppliers of oxygen in this way, and the use of such substances for promoting combustion has long been known. *Touchpaper*, for example, the slowly burning paper which is so familiar in connection with fireworks, is prepared by soaking paper in a solution of saltpetre, and allowing it to dry. The saltpetre is in this way deposited in the fibres of the paper, and renders the latter more readily combustible. Such paper does not require the presence of gaseous oxygen for its combustion, but will burn in an atmosphere of nitrogen or other inert gas. In the case of gunpowder, also, which we shall discuss at a later point (p. 70), saltpetre is similarly made use of as a reservoir of oxygen.

In recent years, the process of combustion by means of combined oxygen has been turned to very good account for the purpose of obtaining economically and with ease, the metals chromium, manganese and titanium, which could formerly be obtained only with considerable difficulty. The metal aluminium, we have seen, has a great affinity

for oxygen, and it combines with great vigour not only with gaseous oxygen but also with the oxygen contained in compounds. If, then, we mix the oxide of chromium with aluminium powder, and strongly heat the mass at one point by means of a special ignition mixture, the aluminium combines with the oxygen of the chromium oxide, and so much heat is thereby generated that the combustion rapidly spreads throughout the whole mass. Oxide of aluminium is formed, and the metallic chromium, which is set free, is fused and collects at the bottom of the vessel. In this way large quantities of chromium are now produced for use, more especially, in the manufacture of a "stainless steel" which does not tarnish in contact with food or acids; and also of a very hard steel known as *chrome steel*. By the introduction of this process, known as the Goldschmidt process, chromium, which twenty years ago cost as much as £25 a pound, can now be obtained for 12*s*. 6*d*. a pound.

A modification of the above process has become familiar in recent years through its application to the welding of tramway rails, and to the repair, *in situ*, of broken castings, shafting, etc., by the so-called thermit process. For this process, oxide of iron is employed instead of oxide of chromium, and the molten iron which is produced, and which has been raised to a temperature of about 5400° F., by the vigour of the reaction, is run into a mould formed round the ends of the rails or fractured metal. The rails are thus raised to such a high temperature that they can be readily welded by pressure, or the fracture is filled with fresh iron and a solid joint effected.

The very high temperature produced by the combustion has also led to the use of thermit mixture in incendiary

bombs designed to be dropped from airships, the bombs being furnished with a special mechanism by means of which the thermit mixture can be ignited automatically.

In order to bring about the various cases of combustion which we have been discussing, it is necessary, as we have seen, to raise the temperature to a certain point, the ignition point. Nowadays this causes no difficulty; and it may be regarded as not the least of the services which chemistry has rendered to man, that it has put it within his power to obtain fire at will, with a minimum both of trouble and expense. From the primitive method of rubbing two dried sticks together to the use of the flint and steel; and from the latter to the modern safety match, is indeed an advance the importance of which for our modern civilisation it would be difficult to estimate and impossible to over-estimate.

One of the characteristics of chemical action, as we have seen it exemplified in the process of combustion, is the production of heat, but it was not till early in the nineteenth century that practical suggestions were made for the employment of such a means of producing fire. One of the earliest of these suggestions which had a certain measure of success was made by a Frenchman named Chancel, who tipped strips of wood with a mixture of potassium chlorate and sugar, bound together by means of gum. When this composition was dipped into concentrated sulphuric acid (oil of vitriol), the sugar took fire and burned at the expense of the oxygen contained in the potassium chlorate; and this combustion was then communicated to the wood splint. These matches were sold as late as the middle of last century. About 1827, John Walker, an Englishman,

patented a match the tip of which consisted of a mixture of potassium chlorate and sulphide of antimony, and this mixture could be ignited by being drawn between folds of glass paper. These matches, known as lucifers, were the first friction matches used.

But there is a substance the use of which for matches is at once suggested both by its name and by its properties, the readily inflammable substance phosphorus, which was discovered as long ago as 1669, and is prepared at the present day from calcium phosphate. From the readiness with which this substance ignites, it was only natural that attempts should be made to utilise it as a convenient fire-producer. Such attempts were at last successful, and phosphorus-tipped matches, known as Congreves, were in almost universal use until a comparatively recent time. The tips of these matches consisted, essentially, of a mixture of phosphorus and some substance rich in oxygen, such as potassium chlorate, or red lead (oxide of lead), bound together with gum or glue, and coloured with various pigments. We can all recollect these matches, which had such a fascination for us in our younger days through the glow of phosphorescent light which they emitted when slightly warmed by rubbing on the hand. As fire-producers these matches were a great advance on those which had gone before. But for every advance a certain price has to be paid, and for the phosphorus match mankind has found the price too heavy. The accidental fires due to the ready inflammability of the phosphorus, and the general danger of its unrestricted use; the number of deaths, accidental or intentional, produced by phosphorus poisoning; and the terrible disease, known as "phossy

jaw," or necrosis of the jaw-bone, which attacked the workers in the match factories, led to a ban being placed on what had been hailed as a boon; and the use of ordinary white or yellow phosphorus [1] has, in most civilised countries, been forbidden by law.

But the element phosphorus occurs not only in the readily inflammable and poisonous white variety, but also in a totally distinct form, that of a dark red powder which is much less readily inflammable and is non-poisonous. It is produced by heating ordinary phosphorus in closed vessels to a temperature of about 480° F. Attempts were therefore made to utilise this form of phosphorus, and the difficulties which were at first encountered, were ultimately overcome by a German chemist about the middle of last century; and his invention, first taken up in Sweden, led to the introduction of the so-called Swedish or safety match. In these matches the red phosphorus is not incorporated in the match head, but is used in the composition with which the rubbing surface is coated. The match tip consists of a mixture of sulphide of antimony and an oxidising substance such as potassium chlorate, red lead, or potassium bichromate; and sulphur and charcoal are sometimes added. This mixture will not take fire when rubbed on a rough surface, but only when rubbed on the specially prepared surface coated with a paste of red phosphorus mixed, sometimes, with sulphide of antimony and powdered glass. Moreover, in order to diminish the risk of accidental fire through the glowing wood of a

[1] Pure phosphorus is a white, translucent, wax-like substance which can be cut with a knife. When exposed to sunlight it becomes yellow or even red in colour owing to its conversion into the so-called red phosphorus.

used match, safety matches are soaked in a solution of alum, sodium phosphate, ammonium phosphate, or some other salt. The charred wood of the match is thereby strengthened, and the match ceases to glow almost immediately after being blown out.

When the use of white phosphorus was forbidden, the attention of chemists was directed to the discovery of other materials which might be used instead, and a non-poisonous match was produced which possessed the advantage of the old phosphorus match, of striking on any rough surface. In the case of this "strike anywhere" match, the tipping composition consists of a mixture of sulphide of phosphorus and potassium chlorate, or other oxidising material, bound together with glue, and powdered glass is also sometimes added to increase the friction and so facilitate the inflammation of the match head.

To render the wood of the match more readily inflammable and so allow of the combustion passing on from the tip to the wood, the latter is impregnated with paraffin wax, although, sometimes, as in the case of some Continental matches, sulphur is employed instead.

In the case of *vesuvians*, the match head consists of a mixture of powdered charcoal and nitre, to which some scenting material, such as gum benzoin or sandal wood, is added. This head is then tipped with a striking mixture such as has already been described.

The making of matches, once a "dangerous occupation," has now passed from the handworker to the machine, which not only cuts the blocks of wood into splints of proper size and shape, but tips them with the inflammable mixture and packs them into boxes, which it also makes

and labels. A single machine can thus turn out over 5,000,000 matches in a day. Only by such means could the almost incredible number of matches be produced which are turned out annually by the match factories of the world. The firm of Bryant and May, the largest British manufacturers, can alone produce, in the course of a year, as many as 90,000,000,000 matches, not to mention wax vestas and tapers, and it has been estimated that the annual consumption of matches in Great Britain amounts to about nine matches per head of population per day.

Although the ordinary match forms by far the most usual means of obtaining fire and light, one must not fail to mention the recently introduced *briquets*, or "cigar lighters." When an alloy of iron and the metal cerium is rubbed against a piece of steel, small particles of the alloy are rubbed off and take fire in the air. If the sparks so produced are allowed to come into contact with a piece of tinder or with the vapour of petrol, or similar volatile liquid, the latter takes fire and we thus obtain a flame. In this apparatus we have, in a refined form, the old flint and steel of our fathers.

CHAPTER III

THE CHEMISTRY OF ILLUMINANTS

AT the present time when, by the mere touch of the finger on a button, we can instantly obtain a flood of brilliant light, it is difficult to realise what must have been the conditions of life when man had to be content with the smoky flame of the pine torch or of the rush dipped in olive oil which burned with but a feeble light even in its vase of finest workmanship. Think also of the old guttering candle, with its constant need of "snuffing," and you will understand how great has been the advance in the direction of artificial illumination; and practically the whole of this advance has taken place since the beginning of the nineteenth century.

The production of light depends in all cases, with the exception of electric light, on the process of combustion in air, and it is therefore only what one would expect, that man first made use of those naturally occurring substances and materials which can be burned without requiring previous special treatment. Thus, the vegetable oils, such as olive oil and rape-seed oil, furnished, from a very early period, the main light-giving material; and at a later date, the need of a vessel to contain the oil was done away with by using the solid animal fats, in the form of candles.

For the earliest candles a solid animal fat was employed, such as ox-fat or tallow, and the candle was made by repeatedly dipping the wick, which was first made from the pith of the rush and later of cotton fibres, into the melted tallow. From the manner in which they were made, these candles were called *dips*.

But early in the nineteenth century, the advance of chemical knowledge enabled man to improve upon nature; the natural was superseded by the artificial, and the task of the careful housewife, who used to save the superfluous kitchen lard for the purpose of candle making, became the business of the manufacturer. This development of the modern candle-making industry we owe to the elucidation by a French chemist, Chevreul, of the chemical nature of fats and oils.

The animal and vegetable fats and oils, so different in outward appearance, are all of the same chemical nature; all are compounds of the familiar substance glycerine ($C_3H_8O_3$), with various acids, such as palmitic acid ($C_{16}H_{32}O_2$), stearic acid ($C_{18}H_{36}O_2$), and oleic acid ($C_{18}H_{34}O_2$). The first two acids are solids and give rise to solid fats; but oleic acid is a liquid, and the glycerine compound derived from it is also a liquid, and the main constituent of olive oil. When, therefore, animal fat or tallow was used in making the old-fashioned dip, the soft material, the glycerine compound of oleic acid, present in varying amounts in the different fats, ran from the burning candle and so caused a wasteful guttering; while the glycerine present in the fat also gave rise, on burning, to an unpleasantly smelling product.

In the making of the modern candle, the fat or tallow is

first boiled with acidified water in order to separate the fibrous matter from the fat, and the latter is then subjected to the action of superheated steam in presence of a little slaked lime, whereby the fat is decomposed into glycerine and the acids with which it was combined—stearic, palmitic and oleic acids. After purification, the mixture of acids is distilled, and the solid acids separated from the liquid oleic acid by pressing. The solid thus obtained consists mainly of stearic acid or stearin, and forms, generally with the addition of a small quantity of paraffin wax, the material of the ordinary stearin candle of the present day. This candle has the advantage over the old tallow dip, in being harder and cleaner to handle, in having a better appearance —white and opaque—in showing no tendency to bend or to gutter, and in burning with a bright and smokeless flame.

The paraffin wax, to which we have just referred, is itself also largely used for making candles. It is a white material which was formerly chiefly obtained by heating in retorts, or distilling, the oil shale found in the Lothians, Scotland. It is now also produced in large quantities in Germany by distilling brown coal or lignite, and is obtained from American and Galician petroleum. It consists of a mixture of compounds which contain only hydrogen and carbon, and are therefore called *hydrocarbons*; it thus belongs to an entirely different class of compounds from the fats or the fatty acids, all of which contain oxygen. Before being employed for the making of candles, the crude paraffin is subjected to a refining process for the purpose of obtaining a wax of higher melting point and free from coloured impurities. The material so

obtained is valued for its slightly translucent appearance, but it has the disadvantage, as compared with stearic acid or stearin, that when exposed to a warm atmosphere, it is liable to bend under its own weight.

The wax candles formerly so highly prized, were made of beeswax, a substance related in its composition to the fats and oils, and consisting mainly of a compound of palmitic acid with an alcohol known as melissyl alcohol. Lastly, spermaceti, a similar compound obtained from the oil of the sperm whale (*physeter macrocephalus*), is another excellent but expensive material used in the manufacture of candles. Candles made of this material have long been used as a standard measure of artificial light, on account of the large and regular flame with which they burn.

Although the materials of which candles are made are, of course, combustible, it should be remembered that they do not burn unless the temperature is raised to a point sufficiently high to cause them to pass into vapour; and it is the vapour which burns and so gives rise to the flame. When a match is applied to the wick of a candle, the small amount of stearin or paraffin which remains in the wick from previous use, is vaporised and ignited, and a bright flame is at once produced. But as the amount of combustible material in the wick is very small, the flame quickly subsides, and it increases again to its normal size only when the heat of the flame has melted a quantity of the solid candle. This liquid then rises up the wick by what is known as capillary action—just as one can mop up water with a piece of blotting paper—and is then vaporised and ignited by the heat of the flame. Moreover, the upward

current of air produced by the flame, cools the surface of the candle so that the upper edge remains solid and so forms a cup in which the liquid produced by the heat of the flame, collects. If the candle is placed in a draught, or if for any other reason the flame does not burn symmetrically, the rim of the cup gets melted away, and the candle "gutters." This is the reason why the ornamental candles with fluted or otherwise moulded surface, however beautiful, while unburnt, they may appear to the eye, do not fulfil the proper function of a candle so well as the plain and unadorned variety.

In the old tallow candles, the wick required to be snuffed from time to time; that is, the unburnt end of the wick had to be removed with a pair of special scissors. The reason for this is as follows. Immediately surrounding the wick of the candle there is the unburnt vapour of the candle material, and this vapour cuts the wick off from contact with the atmospheric oxygen. Consequently, although the wick becomes charred by the heat of the flame, it is not consumed, because the oxygen of the air is not allowed access to it. The charred wick, therefore, continues to increase in length and there is conducted up into the flame more of the liquid fuel than can properly be consumed. The flame then burns dim and emits a large amount of smoke. One can readily understand how all the trouble and inconvenience of the constant snuffing could lead a Goethe to declare, in words which may be rendered thus—

> There could be no greater discovery made,
> Than of candles to burn without snuffers' aid.

And this discovery was made by the Frenchman

Cambacères in 1825, the necessity for snuffing being obviated by the use of twisted or flat plaited wicks. As the candle burns, the end of the wick, as everyone may see by looking at a burning candle, curls or bends outwards to the edge of the flame, and coming, in this way, into contact with the oxygen of the air, it burns away, and so no snuffing is required. But if the best results are to be obtained, the manufacturer must pay great attention to the proper selection of the wick as regards its size and texture in relation to the material of the candle; and care also must be given to the proper treatment or "pickling" of the wick with saltpetre or other chemicals, in order to prevent smoking and the formation of an ash.

In its fight with other illuminants, the candle dies hard; indeed, it does not die at all, for the consumption of candles goes on increasing. Convenience in use, especially in mines; poetic sentiment and an age-long tradition which have made the candle the type of all light-bearers; as well also as æsthetic and economic considerations, all conspire in favour of the candle. In Great Britain alone, between 40,000 and 50,000 tons of candles are consumed annually, by far the greatest proportion of these being paraffin candles.

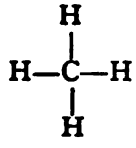
In the southern districts of Scotland there occur deposits of shale which, when heated in retorts out of contact with the air, yields the white paraffin wax to which we have already referred. But besides this, large quantities of liquid oil are also produced which, in the early days of the industry, was a by-product of comparatively little value. But the oil was bought, bought indeed at a low price, and shipped to Germany; and when its use there was investigated,

it was found that a special lamp had been invented in which the oil was used as an illuminant. So commenced the use of mineral oil for the production of light. Soon, however, this Scottish industry was seriously threatened by the discovery and exploitation of oil deposits in America, Russia and other parts of the world; but it fought for its life, fought with the only weapons which were of any avail, the weapons of science, and it prevailed. And we have in Scotland, in the life of the oil shale industry, a striking testimony to the power of science in its practical applications.

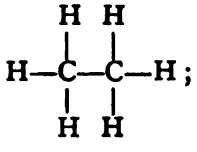
When one stirs the mud of decaying vegetation at the bottom of a stagnant pool, bubbles of a gas rise up, and on holding a light near the surface of the water the gas takes fire. This inflammable gas, from its occurrence in marshy districts, has long been known as marsh gas. It is this gas, also, which, escaping from the coal beds during mining, mixes with the air of the colliery and constitutes the explosive mixture fire-damp. Marsh gas, or methane as it is called in chemistry, is also the main constituent of the combustible gas which escapes from the earth in various oil-bearing regions in America, and in the region of Baku on the Caspian Sea, where the Holy Fire of the burning gas was for long a place of pilgrimage of the Persian Guebers, or fire-worshippers. To-day all this is changed. "The worship of the Eternal Fire in the Surakhani temple is dead; the priest has left behind no followers; but the oil that dimly lit a shrine now illuminates an empire, and bids, ere long, to give light and heat to an entire hemisphere."[1]

[1] Marvin, "The Region of the Eternal Fire." 1884.

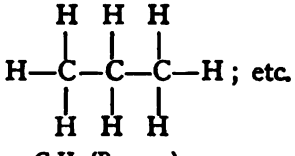
Methane, or marsh gas, is the lowest member of a long series of hydrocarbons (the name given to compounds composed entirely of hydrogen and carbon), all of which have similar chemical properties and composition. The molecule of methane consists of one atom of carbon to which four atoms of hydrogen are united; and since an atom of carbon is never found to combine with more than four atoms of hydrogen, the carbon is said to be saturated, and methane is spoken of as a *saturated hydrocarbon*. Diagrammatically, we can represent the molecule of methane thus:



But the element carbon is remarkable among all the elements in its property of combining also with other atoms of carbon, and so forming "chains" of carbon atoms, so that a series of compounds is obtained which may be represented by the diagrams:



C_2H_6 (Ethane).

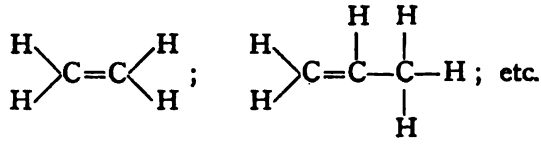


C_3H_8 (Propane).

A large number of such compounds are known, and it will be observed that we can represent the composition of each of them by the formula C_nH_{2n+2}.

It may also be mentioned here that other hydrocarbons are known which contain a lower proportion of hydrogen,

and are therefore said to be *unsaturated*. Thus, if we take away two hydrogen atoms from each of the compounds of the methane series, we obtain hydrocarbons which we can represent by the formulæ:



C_2H_4 (Ethylene). C_3H_6 (Propylene).

These constitute another series of hydrocarbons, known by the name of the first member ethylene. As we shall see, this gas plays an important part in coal gas.

Hydrocarbons are also known which contain a still lower proportion of hydrogen, or higher proportion of carbon, for example acetylene, C_2H_2 or $HC \equiv CH$, the first of a series having the general formula C_nH_{2n-2}.

American petroleum consists mainly of a number of hydrocarbons belonging to the methane series, from CH_4 up to $C_{30}H_{62}$; but the petroleum obtained in Southern Russia contains also a number of hydrocarbons belonging to a different series with a lower proportion of hydrogen, and more akin to the substance benzene. These naturally occurring mineral oils, then, formed by the gradual decomposition of marine animal and vegetable matter under the age-long action of heat and pressure, are not single substances but mixtures of a large number of different compounds, the lowest members of which are gases which escape from the earth as "natural gas." As the proportion of carbon in the compounds increases, the hydrocarbons become less and less volatile, and boil, therefore, at higher and higher temperatures; and when the number of carbon

atoms in the molecule is greater than sixteen, the compounds are solid at the ordinary temperature.

When the crude petroleum is distilled (Fig. 3), the lower and more volatile hydrocarbons pass over first; and by collecting the liquid which distils over at different temperatures, a series of "fractions," as they are called, is obtained. The liquid which distils over between the temperatures of 120° and 140° F., is called petroleum ether, and is largely used as a solvent; the fraction distilling over between 160° and 190° F., is called gasoline or petrol,

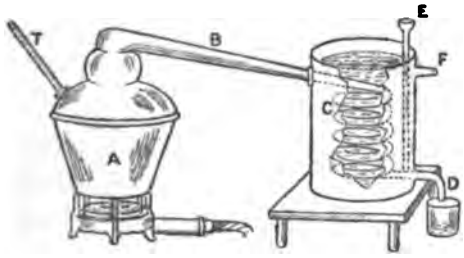


FIG. 3.—APPARATUS USED FOR DISTILLING LIQUIDS.

A, a vessel in which the liquid is boiled and so converted into vapour which passes through the long neck, B, to a spiral "worm," or condenser, C, kept cold by means of flowing water. The condensed vapour issues at D and can be collected. E, tube through which cold water enters; F, exit for warm condenser water; T, thermometer to indicate the temperature of the vapour.

and finds extensive use in the engines of motor cars, and also for illuminating purposes (petrol-air gas); while the fraction distilling between 250° and 300° F. is called benzine (not benzene) or benzoline, and is used as a "dry cleaning" agent, for the removal of oil and grease stains from leather, cloth, etc.

As the temperature of distillation rises, the hydrocarbons of higher boiling-point distil over. The fraction distilling between 300° and 570° F., constitutes burning oil

or kerosene, while from the higher fractions one obtains lubricating oils, vaseline, and in some cases, solid paraffin, which is used for making candles, waterproofing paper, and other purposes.

Since paraffin oil, or kerosene, contains a relatively large proportion of carbon, it burns with a smoky flame, owing to incomplete combustion, unless there is a liberal supply of air. When this oil is used as an illuminant, therefore, the flame is surrounded by a chimney whereby a draught of air is created and oxygen thus brought in larger amount to the flame; and in the case of lamps with a circular wick, a tube must also be provided through which air can pass to the *inner* surface of the flame.

In the early days after the introduction of mineral oil as an illuminant, explosions and fires were not infrequent, and these led to the introduction of special legislation to regulate the use of such oil. The accidents which occurred were due mainly to the insufficient removal of the more volatile constituents of the petroleum, and these, mixing with the air in the oil reservoir of the lamp, formed an explosive mixture which became ignited by the flame. To obviate such risks, it has been enacted that only such oil shall be used as does not give off an inflammable vapour below a certain temperature. This is tested by heating the oil in a special apparatus under specified conditions, and determining the temperature at which, on passing a light over the mouth of the vessel containing the oil, a flash of flame is seen. This is known as the flash-point of the oil, and in Great Britain it has been enacted that the flash-point must not be below 73° F., when determined by what is known as the "closed" test.

By far the most important illuminant at the present day is the gas obtained by heating coal in a closed vessel or "retort," out of contact with the air. That a combustible gas can be produced in this way has long been known, but it is to a Scotsman, William Murdoch, that belongs the credit of having developed the process for the production of an illuminating gas for general use.[1] That was towards the end of the eighteenth century, but it was only after the lapse of ten or twelve years that the gas began to be publicly and generally used. The great change which was thereby effected in the appearance of the towns and in the comfort of the people, is described by a writer in the early nineteenth century: "We all remember the dismal appearance of our most public streets previous to the year 1810; before that time, the light afforded by the street lamps hardly enabled the passenger to distinguish a watchman from a thief, or the pavement from the gutter. The case is now different, for the gas-lamps afford a light little inferior to daylight and the streets are consequently divested of many terrors and disagreeables, formerly borne with because they were inevitable."

When we recall what street illumination was like in our own times, before the introduction of the incandescent mantle and electric light, the fact that the writer just quoted could regard the light afforded by the gas-lamps of the early nineteenth century as being little inferior to daylight, must certainly convince us that "the appearance of our most public streets previous to the year 1810"

[1] William Murdoch was associated with the engineering firm of Messrs. Boulton and Watt, Birmingham, and it was in their works at Soho that coal gas was first used (in 1798) on a large scale as an illuminant.

must have been very dismal indeed. And yet the cry is for light and still more light.

Coal is not a definite chemical substance, but a complex mixture of substances, the nature of which is not yet definitely known. The essential elementary constituents of coal are carbon, hydrogen, and oxygen, but the elements nitrogen and sulphur also occur in small amounts; and when coal is heated in closed retorts, or "distilled" as one says, there is obtained not only the gas which is used for illuminating purposes, but also considerable quantities of ammonia and of tar, and there remains in the retort a residue of coke. Half a century ago, the ammonia and the tar were regarded as by-products of little value, but, as we shall learn more fully later, they have more recently acquired an importance but little inferior to the illuminating gas itself;[1] while, owing to the great developments of the iron and steel industry, the demand for coke has, in recent times, become so great, that many millions of tons of coal are now distilled annually for the production, primarily, not of gas but of coke.

Although the nature of the products as well as their relative amounts depend on the kind of coal distilled and on the temperature at which the process is carried out, we may say that, under the general conditions met with in gas works, the main products obtained and their relative amounts are as follows:—

	Approximate quantity formed from 1 ton of coal.
1. Illuminating gas	11,000 cubic feet.
2. Coal tar	120 lbs.
3. Ammonium sulphate	25 ,,
4. Coke	1500 ,,

[1] In some cases the value of the ammonium sulphate recovered as a by-product may equal or even exceed the cost of the coal distilled.

In the manufacture of illuminating gas, the coal is heated in large fire-clay retorts at a temperature of about 1800° F., and the products of decomposition are led away by a pipe the mouth of which dips under the surface of water contained in what is known as the hydraulic main (Fig. 4). Here, part of the water and of the coal tar condense, while the gaseous products pass away to a series of cooling pipes, exposed to the air, in which a further condensation of water vapour and of tar takes place. The ammonia present in the gas dissolves for the most part in the water produced, and the remainder is removed by passing the gas through "scrubbers." The gas still contains a number of substances the presence of which would be deleterious, the more important of these being sulphuretted hydrogen and carbon dioxide. The sulphuretted hydrogen is harmful because it gives rise, in the burning gas, to sulphur dioxide (the pungent gas formed when sulphur burns in air), which exercises a destructive action on plants, furniture, etc.; and the presence of carbon dioxide is objectionable because it lowers the illuminating power of the gas. To free the gas from these impurities, therefore, it is passed, first of all, through a series of boxes containing trays covered with slaked lime which combines with and so removes the carbon dioxide; and then through another series of boxes containing oxide of iron, which removes the sulphuretted hydrogen, by forming with it the compound sulphide of iron. When conversion of the oxide into sulphide is complete, the material is incapable of removing any more sulphuretted hydrogen, but it can be revivified by exposure to the air. Through this exposure, the oxygen of the air reconverts the sulphide of iron into

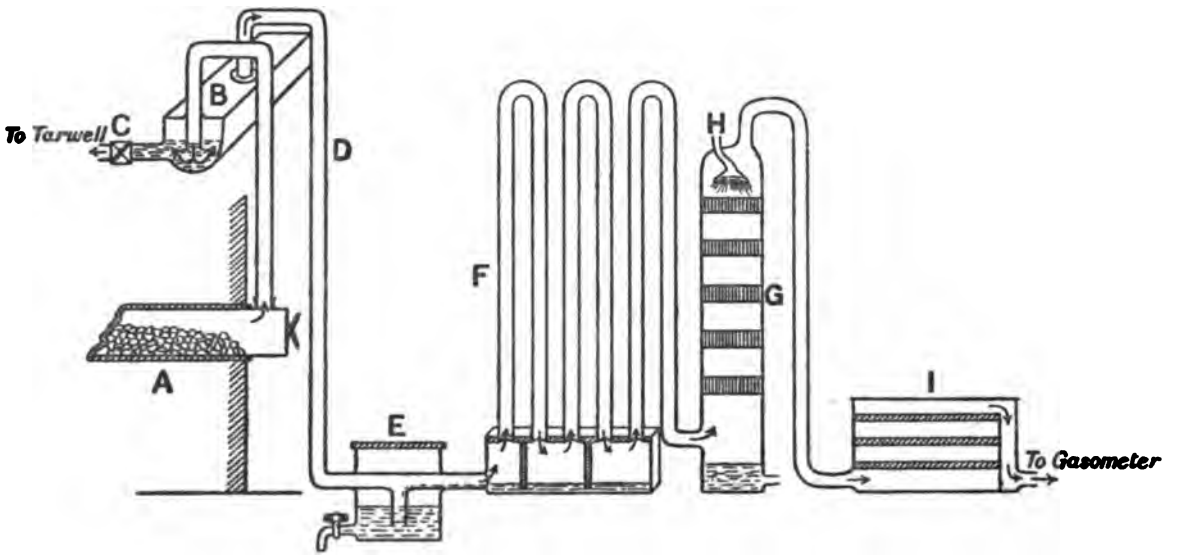


FIG. 4.—DIAGRAM OF GAS-MANUFACTURING PLANT.

A, retort in which coal is heated; B, the hydraulic main; C, outlet for the tar; D, gas pipe; E, tank in which the ammoniacal liquor collects; F, cooling pipes; G, scrubber in which traces of ammonia are removed by trickling water, supplied through the sprinkler H; I, purifying boxes for removing carbon dioxide and sulphuretted hydrogen.

oxide of iron, and the sulphur is set free. In this way the oxide of iron may be used repeatedly, until at length the accumulation of sulphur renders it inefficient. The material, however, still has its uses, for it is sold to the manufacturer of sulphuric acid who utilises it in the manner we shall learn later.

After undergoing the various processes of purification, the illuminating gas passes to the gasometer, and is then ready for distribution to the consumers. Although the composition of the gas supplied by different works is by no means the same, nor invariable even in the case of the same works, the following numbers may be taken as representing an average composition of illuminating gas.

COMPOSITION OF COAL-GAS

Hydrogen	49	per cent.	by volume
Methane	35	,,	,,
Unsaturated hydrocarbons (Ethylene, etc.)	4	,,	,,
Carbon monoxide	5	,,	,,
Carbon dioxide	0·5	,,	,,
Nitrogen	6	,,	,,
Oxygen	0·5	,,	,,

Coal-gas, then, as we see, is a mixture of a number of gases, and of these carbon dioxide, nitrogen, and oxygen represent what we may call impurities; they act merely as diluents and lower the illuminating power of the gas.

Of the combustible gases present in coal-gas, hydrogen burns with a non-luminous, scarcely visible flame; carbon monoxide, with a non-luminous flame of a bright blue colour;[1] and methane, with a flame which has only a slight illuminating power. Ethylene, however, burns with a

[1] The lambent blue flame seen on the top of a clear-burning fire, is due to the combustion of carbon monoxide.

strongly luminous flame, and it is to this gas, and to the other unsaturated hydrocarbons present in small amounts, that the luminosity of a coal-gas flame is mainly due. Among the unsaturated hydrocarbons present, there may be mentioned benzene (or benzol, to give it the name by which it is known in commerce), the vapour of which burns with a luminous flame and with the production of a large amount of soot.

What, then, is the explanation of the luminosity of the flame of burning coal-gas, or of a candle, or petroleum? The answer is that which was given long ago by Sir Humphry Davy: The luminosity depends on the decomposition of the hydrocarbons with liberation of particles of carbon which are then raised to incandescence by the heat of the burning gases. The presence of this finely divided carbon can, indeed, be readily shown by bringing a cold object into the luminous part of the flame; it becomes coated with soot. These carbon particles, however, do not escape into the air, but on reaching the edge of the flame where they come into contact with the oxygen of the air, they are completely burned to the invisible gas carbon dioxide. And so, on examination, we see in these flames three zones: an inner non-luminous zone of unburnt gas or vapour; a luminous zone in which the carbon particles are raised to incandescence; and a very faint outer zone surrounding the flame, in which complete combustion of the carbon particles takes place.

From the explanation which has just been given, it will readily be understood that the luminosity of a flame will be increased by increasing the proportion of carbon-yielding substances in the burning gas; and hydrocarbons, and

more especially unsaturated hydrocarbons, which contain a relatively large proportion of carbon, will be the most effective substances to use. By such additions it is possible to "enrich" a poorly luminous gas, a fact which is made use of at the present day in many of the larger gas works.

Not only can a combustible gas be manufactured by the distillation of coal, but when steam is passed over red-hot coke, a gas is obtained which is a mixture of hydrogen and carbon monoxide:

$$C + H_2O = CO + H_2$$

Carbon (coke) and water give carbon monoxide and hydrogen.

Although this gas mixture, known as *water gas*, has no illuminating power, it can be manufactured at a small cost, and after being enriched by the addition of unsaturated hydrocarbons, obtained by the decomposition or "cracking" of oil at a high temperature, it is added (as *carburetted water gas*) to the gas obtained by the distillation of coal.

If the coal-gas, before being burned, is mixed with a suitable amount of air, the molecules of the combustible gas find oxygen with which they can combine, ready at hand, so to say, and combustion takes place rapidly and completely without the separation of carbon particles; the flame is therefore non-luminous, but much hotter than the ordinary luminous flame. This principle was made use of by the German chemist Bunsen in the burner which goes by his name, and is applied in gas fires, gas cookers, etc. (Figs. 5 and 6). In the Bunsen burner, the gas issues from a jet which is surrounded by a wider tube, near the foot of which holes are pierced through which air is drawn into the burner by the uprush of gas. The gas

thereby becomes mixed with air, the amount of which necessary to ensure complete combustion can be regulated by enlarging or diminishing the size of the air openings. If too much air is admitted to the gas, the mixture becomes explosive, and the flame strikes back to the jet where the gas enters the burner. If this occurs, the gas must be at once turned out, as incomplete combustion takes place and products of a very poisonous character are formed. These, fortunately, betray their presence by a powerful and unpleasant odour.

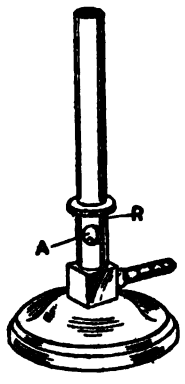


FIG. 5.—BUNSEN BURNER.

A, air-hole by which air can pass into the tube and mix with the gas which enters at the small jet seen through the opening. The supply of air can be regulated by means of the movable ring R.

If, instead of supplying the luminous coal-gas flame with air, we supply it with oxygen, a still better result, that is, a greater production of heat, and therefore a higher temperature, can be obtained; for the nitrogen of the air acts merely as a diluent and so cools down the flame. We cannot, however, in this case make use of the ordinary burner, for the mixture of oxygen and coal-gas would be explosive, and the flame would at once "strike back." A burner of special construction is therefore employed which allows of a jet of oxygen being blown into the gas as it burns at the mouth of the burner, and we thus obtain what

FIG. 6.—GAS COOKER, CONSTRUCTED ON THE PRINCIPLE OF THE BUNSEN BURNER.

is known as the oxy-coal-gas blowpipe flame (Fig. 7). If this flame is allowed to impinge on a highly refractory material like quicklime, the latter is raised to a brilliant incandescence, producing the well-known lime-light. (Nowadays, the oxide of the rare metal zirconium is largely used in place of lime.)

The high temperature produced by means of the oxy-coal-gas flame[1] has recently found an interesting and important application in the manufacture of artificial gems, such as rubies and sapphires. These gems consist essentially of oxide of aluminium (alumina), a substance which occurs naturally as corundum, and, in an impure state, as emery. It is a very refractory substance, but it can be melted in the oxy-coal-gas blowpipe flame. When a mixture of 97·5 per cent. of alumina and 2·5 per cent. of oxide of chromium is heated in the blowpipe flame, it is fused, and, on cooling, solidifies in the crystalline form of the ruby. It *is* a ruby, identical in physical and chemical properties with the natural gem; and it differs from the latter solely in minute irregularities of internal structure detectable only by the eye of the expert. In the manner

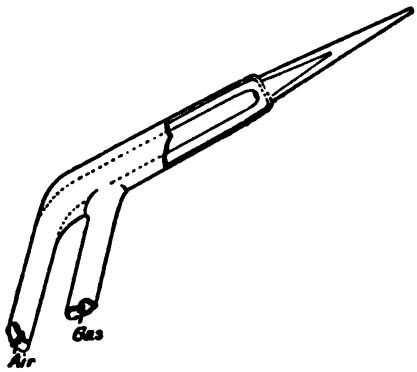


FIG. 7.—BLOWPIPE.

When the gas is burning at the mouth of the wider tube, air or oxygen is blown into the flame through the inner tube.

[1] If hydrogen is used in place of coal-gas, a still higher temperature, up to about 3600° F., can be obtained.

described, artificial rubies weighing as much as eighty carats, or over half an ounce avoirdupois, have been obtained; and they can be purchased uncut at about 8*d.* per carat, and at 5*s.* per carat cut as a gem. These artificial rubies, on account of their great hardness, are now manufactured in large quantities for use in the bearings of watches and for other purposes.

Sapphires can be obtained in a similar manner by fusing a mixture consisting of alumina and small quantities of the oxides of titanium and iron.

For a number of years the position of coal-gas as an illuminant has been persistently assailed by electricity; and it is very doubtful if the industry could have maintained itself but for the invention of the now familiar incandescent mantle.

It is a proverbial saying that necessity is the mother of invention, but we should miss the real lesson which the incandescent mantle should convey to us, if we allowed ourselves to think that it was invented under the pressure or the stimulus of necessity or out of the conscious desire to improve the illuminating efficiency of gas. Some, indeed, had laboured with that end in view, but they laboured in vain, and we owe the incandescent mantle, with all its enormous economic and industrial consequences, to a purely scientific investigation of the oxides of the rare metals which was carried out by Auer von Welsbach in the laboratory of Bunsen at Heidelberg, in 1884.

In the course of his investigations, von Welsbach was struck by the fact that some of the oxides of the rare metals emitted an exceptionally brilliant light when incandescent;

and at once his mind grasped the potentialities of the fact. A scientific discovery, however, is one thing; to make that discovery of practical utility is quite another; and in the present case, as in all cases, a large amount of patient and careful investigation had to be carried out before the incandescent mantle could be made a commercial success and be brought to its present state of perfection. How great has been its success, into what an enormous industry a single observation may develop, although made in the course of an investigation having apparently no practical importance, is clearly seen from the fact that the world's annual consumption of incandescent mantles has been placed at about 300,000,000.

Let us take the lesson of that discovery and of its application to heart.

To make the discovery of practical utility, "mantles" or "stockings" of woven cotton or, as is now generally used, ramie fibre (fibre produced from a plant of the nettle class), are soaked in a solution containing the nitrates of thorium and cerium[1] in the proper proportions. These mantles are then dried and incinerated, whereby the fibre is burned away and the nitrates are converted into a mixture of the oxides of the metals, which form a skeleton work preserving the shape of the mantle. On suspending this in the hot, non-luminous flame of a special burner constructed on the principle of the Bunsen burner, the mantle is raised to incandescence and emits a brilliant white light, about four times brighter than is given by the old flat flame consuming the same amount of gas. From a careful investigation

[1] The chief source of these elements is a mineral known as monazite, which is found in various parts of the world, but more especially in Brazil.

it was found that the best results are obtained when the oxides are present in the proportion of 99 per cent. of thoria (thorium oxide) to 1 per cent. of ceria (cerium oxide). Neither thoria itself nor ceria itself has much light-giving power; and any variation in the proportions of the two oxides from those given, is accompanied by a diminution in the light-giving power of the mantle. The part played by the small quantity of ceria in the mantle is, therefore, a very important one, for which, however, no completely satisfactory explanation has yet been found.

The most plausible explanation so far advanced is that the particles of ceria are embedded in a badly conducting mass of thoria, which allows of the ceria being heated up to a point of brilliant incandescence; and further, the ceria possesses the property of accelerating the combustion of the gas, so that the combustion is concentrated or focussed on the small particles of ceria. As a consequence, the temperature of these particles rises above the average temperature of the mantle, and the brightness of the incandescence is thereby increased. This action of the ceria is spoken of as a *catalytic* action, about which we shall have more to say later on. Ceria, however, is a substance which radiates heat rapidly, and if present in the mantle in larger amounts, the loss of heat by radiation is so great that the catalytic action is more than counterbalanced, and the illuminating power of the mantle is diminished.

The invention of the incandescent mantle completely revolutionised the gas industry. Not only could a very bright light, rivalling that of the electric incandescent lamp, be obtained, but the cost of production of the gas

was lowered because it was found that equally good results could be obtained with a gas of poorer quality, that is, of lower illuminating power. Gas manufacturers, therefore, were able to use cheaper coal, and, by carrying out the distillation at a higher temperature, were able to obtain a larger volume of gas from the coal. Although the illuminating power of this gas when burned in a flat flame is lower than formerly, the temperature produced in the flame, and therefore the incandescence of the mantle, are not greatly affected.

One other illuminant must be mentioned, the use of which depends on the process of combustion in air, namely, acetylene, a gas which is readily obtained by the action of water on a compound of calcium and carbon, known as calcium carbide. This substance is obtained by heating to a high temperature a mixture of quicklime (calcium oxide) and carbon in the form of anthracite coal or coke. The preparation is carried out in a special type of furnace in which the high temperature necessary is obtained by means of the electric arc,[1] and owing to its use for the production of acetylene and for other purposes, carbide is now manufactured in large quantities in most civilised countries.

Acetylene is an unsaturated hydrocarbon, having a relatively large proportion (over 92 per cent.) of carbon, as is shown by its formula C_2H_2 (cf. p. 13). Under ordinary conditions the gas burns with a luminous and very smoky flame, but by using a special burner which

[1] A temperature estimated at between 5000° and 6000° F. can in this way be obtained.

ensures the admixture with the gas of a small amount of air, a white, intensely luminous flame is obtained.

By injecting oxygen into a flame of acetylene, a temperature of over 5000° F. can be obtained, and this fact has received important applications. If, for example, the oxy-acetylene flame is allowed to impinge on a piece of iron, the metal is heated locally to redness, and if a fine jet of oxygen is then directed against the red-hot metal, the iron is oxidised to oxide of iron which melts in the intensely hot blowpipe flame, and flows away like water. By this means one can cut through even large rods, shafts, or girders as easily as a knife will cut through cheese, and with a cut almost as fine. The oxy-acetylene blowpipe flame was, in fact, used in this way with great effect to cut through the dense tangle of iron girders formed by the collapse of the buildings in the fire at the Brussels Exhibition of 1910.

CHAPTER IV

ENERGY, FUEL, AND EXPLOSIVES

THE consideration of the process of combustion, controlled and utilised for the production of light, leads us to the realisation of the fact that in the chemical reactions and transformations which take place, we are not dealing merely with material things. In the case of the burning candle, oil, or coal-gas, it is not the material substances — the stearin, paraffin, hydrogen, methane, etc.—which interest us primarily, nor the products of combustion, the carbon dioxide and the water vapour but the immaterial light, the ethereal vibrations to which the process of combustion gives rise. So also, passing on to the consideration of combustible substances as fuels, and of the process of combustion as a source of heat, we again recognise that our interest is focussed not on the material nature of the combustibles, but on their efficiency as heat-producers. Heat, however, is a form of energy, and can be converted into other forms of energy, such as mechanical energy, and can perform what we call work; and so it is really in their power of doing work that we see the value of combustibles. The combustible substances together with the oxygen of the air, represent so much potential energy, and the process of combustion is

like the downward rush of the waterfall in being a process by which potential energy becomes available for doing work. In the recognition of the supreme importance of energy, in the establishment of the law of the conservation of energy and of the laws governing the mutual transformation of the different forms of energy, we see the crowning achievement of nineteenth century physical science; and if one would grasp the spirit of modern chemistry, one must learn to regard a chemical change or reaction not merely as involving some material transformation but as representing a flow of energy out of or into the substances undergoing the change. "Real gain," as Sir William Ramsay said some years ago in his presidential address to the British Association, "real gain, real progress consists in learning how better to employ energy—how better to effect its transformation"; and it is by the utilisation of energy and by the methods of applying and transforming energy, that the nineteenth and twentieth centuries are so strongly marked off from the centuries which preceded them.

At the present day by far the greatest part of the energy necessary for the continuance of vital activity, as well as for carrying on the industrial life of the world, is derived from the energy of combustion of carbon, and of its compounds. Through the oxidation of carbonaceous food by means of the oxygen taken in through the lungs, the vital activity of the animal organism is maintained, and the inert carbon dioxide produced in the process is sent into the atmosphere in the expired air. But the carbon does not thereby cease to be available, for the green plants, absorbing the radiant energy of sunlight,

transform and utilise the carbon dioxide for the purpose of building up their own structures and producing compounds like starch and sugar, which again become the food and the source of energy of animals. In the case, therefore, of the element carbon which constitutes the basic element of all life, we find a continual circulation in nature, whereby the mutual preservation of the animal and vegetable worlds is secured. The green plants act as transformers of the radiant energy of sunlight into the potential energy of combustible substances.

Until comparatively recent times, down, say, to the thirteenth century, wood was the almost universal fuel; but since coal first began to be mined, it has become, in an ever-increasing degree, the immediate source of the energy on the utilisation and transformation of which our present-day civilisation depends, and it now occupies a position of unquestioned pre-eminence.

Coal consists of the fossil remains of early, luxuriant vegetations. Through an age-long process the cellulose of which the woody fibre essentially consists, has become converted into more highly carbonised compounds, the proportion of hydrogen and oxygen becoming diminished owing to the formation of gaseous substances such as carbon dioxide and marsh gas. From the figures given in the following table, we can recognise the gradual carbonisation of cellulose, the materials peat, lignite or brown coal, bituminous coal, and anthracite representing progressive stages in the natural process.[1]

[1] It must be noted that wood, peat, and coal are not definite chemical compounds, and that the composition of the different kinds of coal may vary considerably. The numbers given in the table, therefore, are only approximate values representing, as it were, the composition and calorific value of

	Carbon.	Hydrogen.	Oxygen.	Calorific value B. Th. U. per lb.
Cellulose ($C_6H_{10}O_5$) .	44·5	6·2	49·3	7500
Wood	50·0	6·0	44·0	7400
Peat (Irish).	60·0	5·9	34·1	9900
Lignite	67·0	5·2	27·8	11,700
Bituminous coal . .	88·4	5·6	6·0	14,950
Welsh steam coal . .	92·5	4·7	2·7	15,720
Anthracite	94·1	3·4	2·5	

The process of carbonisation is accompanied by a diminution of the amount of gaseous and volatile matter which the fuel can yield on being heated, and this markedly affects the manner in which the different materials burn. Dry wood, we know, burns readily and with a bright and cheerful flame, whereas anthracite, which represents the most advanced stage in the natural process of carbonisation of woody fibre, is ignited only with difficulty, and burns with a very small and not strongly luminous flame.

But it is not with the cheerfulness with which the fuel burns that we are concerned here, but with the all-important question of how much heat, how much energy is given out in the process of combustion. It is the "calorific value" of the fuel that claims our attention just now.

When we examine the different solid fuels from this point of view we find, as the figures in the last column of the table given above show, that with the progressive carbonisation, the heat-producing power of the fuel increases, so that among all the solid fuels, anthracite stands

an average member of the different classes. Moreover, other substances, more especially nitrogen, are present, besides carbon, hydrogen, and oxygen, and although, under certain conditions, these substances may give rise to important by-products, their influence on the fuel value of the combustible materials is very small.

pre-eminent. A British thermal unit represents the amount of heat required to raise the temperature of one pound of water through 1° F., and the numbers in the table show that whereas one pound of wood will give out, on burning, about 7400 units, an equal weight of bituminous or household coal will yield about 14,900, while Welsh steam coal and anthracite will give 15,700, units. Hence the importance which we attach to our supplies of Welsh steam coal and anthracite.

A consideration of these calorific values will, perhaps, also help to convince us how unscientific, how irrational it is to buy coal, as we do, merely by the weight without regard to the amount of heat which the coal can give out. It is true that the existence of different kinds of coal having varying quality or calorific value, is recognised to some extent by a variation in the price charged; but what is, perhaps, not sufficiently recognised is that there may be considerable variation in the heat value of even the same kind of coal, or of coal drawn at different times from the same mine. If we could only realise more thoroughly that when we buy coal we do so not for the sake of the material itself, but for the energy which can be obtained from it, we should soon, I hope, everywhere adopt the practice, which is common in the United States and on the Continent, of purchasing our coal not merely by weight, but with some consideration of its heat-producing value, a certificate of which the sellers of the fuel might be made to provide.

During the past fifty years there has taken place throughout the world an enormous increase in industrial production, and the great river of energy which has thus flowed through

the channel of industry, has had its source mainly in coal. The control and direction of such a flow of energy is a matter on which man may legitimately congratulate himself. But is there not also some cause for anxiety? What of the future? The world's supply of coal, this "bottled-up sunshine," on which the whole of our boasted civilisation depends, is being used up with an almost appalling rapidity; and although, no doubt, the storing up of the sun's energy is going on now as in the past, the rate at which coal is being formed is so incomparably slower than that at which it is being consumed, that it can only be a question of time when the coal supply will become exhausted.

In this country the natural stock of coal is being depleted at the rate of nearly 290,000,000 tons per annum, and the rate increases rather than diminishes. How long can this go on? With regard to this point, there must inevitably be some uncertainty, and authorities are divided in their opinion. But even if we double the estimate of 175 years, the period—350 years—is not a very long one in the history of the nation. At the end of that time our reserves of coal will be exhausted and the industries on which our national life and civilisation so largely depend, will be imperilled or destroyed. It is therefore of the highest national importance that everything possible should be done to avoid waste of our irreplaceable supplies of coal, and to seek for and develop all other available sources of energy.

How then can we delay the exhaustion of our coal supply, and so preserve this life-blood of our industries? Can we, by altering the manner in which we burn our coal, procure a better utilisation of the energy and thereby effect

a saving of the fuel? The problem is a very complex one and a detailed consideration of it would carry us far beyond the limits of our present discussion. Anything in the nature of a violent revolution is scarcely possible, and perhaps not advisable; but that the public mind should become alive to the call for a reform, is imperative in the interests of the country as a whole. That a check should be placed on the wasteful use of the irreplaceable reserves of energy, of which we are the stewards, is a matter which should appeal, if not to the moral sense of the nation, then surely to that scientific conscience which the stress of the times is slowly awakening into life.

When we consider merely the case of domestic heating, in which about forty million tons of coal are consumed annually in Great Britain, we have to confess that the British open fire is a most wasteful method of heating. When fresh coal is put on a fire, a process of distillation takes place with production of gas and tarry products which, undergoing a partial decomposition with separation of carbon, give rise to clouds of smoke. Thereby, it has been shown, as much as a third of the heating value of the coal is lost.

But if the open fire is wasteful we shall not willingly consent to give it up, and we may place against its wastefulness, its efficiency in promoting ventilation and the hygienically advantageous manner of heating by radiation. Moreover, its comfortable appearance, "the wee bit ingle blinkin' bonnily," is something which has a value of its own, not recognised perhaps by science, but which doubtless reacts powerfully on the temperament and character of the people. Attempts therefore have been made to produce

a fuel which can be burned in the open fire and which, by avoiding the waste accompanying the production of smoke, would not only effect an economy but would also do much to abate the "smoke nuisance." By carrying out the distillation of coal in retorts one can avoid the most wasteful part of the process of burning coal in the open fire, for the illuminating gas and the very valuable ammonia and tar are collected, and the coke which is left behind can be used as a smokeless fuel. Although the ordinary coke of the gas-works is such that it cannot be burned readily in the open fire, it has been found that by carrying out the distillation of the coal at a lower temperature, the residual coke still contains sufficient volatile matter to enable it to burn readily and without smoke in the ordinary grate. Coalite, for example, of which much was recently heard, and of which, or of similar material, much will doubtless be heard in the future, is a smokeless fuel of this description.

But another way in which economy can be effected, especially in towns, is by the use of gas for heating and cooking purposes, and recent years have, indeed, seen a very great development in this direction. Many improvements, also, have been effected in the construction of gas fires so that their ventilating efficiency and their emission of radiant heat have been greatly improved, and they have now lost practically all their former unhygienic properties. Moreover, owing to the introduction to a greater extent of the chemist into gas-works, improvements have been brought about not only in the actual methods of gas manufacture, but also in the recovery and use of the by-products, so that gas can in some cases effectually compete with coal even when used for continuous heating. The

more general use of gaseous fuel would doubtless be greatly encouraged by an alteration of the municipal regulations. In most cases these prescribe a certain standard of illuminating power, but at the present time, when incandescent mantles are in almost universal use for gas lighting, and when gas is so much employed for heating and cooking purposes, it is not the illuminating power but the heating power of the gas that is of importance. And since the cost of producing a gas of high illuminating power is greater than that of manufacturing a gas of almost equal heat value but lower illuminating power, the present regulations, by increasing the cost of production, exercise a certain restraint on the increased use of gas for heating purposes.

In the industrial use of coal, also, there is room for very considerable improvement. Great economies can be and have been effected by the installation of more efficient furnaces, and by the more careful control of the air supply; and a still greater saving can in many cases be effected by replacing the very inefficient steam engine by the far more efficient gas engine. For driving such engines one can employ not only the ordinary illuminating gas obtained by the distillation of coal, but also other combustible gases which can be produced more cheaply. Thus *water gas*, obtained by passing steam over red-hot coke, and consisting essentially of carbon monoxide and hydrogen; *producer gas*, obtained by passing air over red-hot coke, and consisting of carbon monoxide and nitrogen; *Mond gas*, obtained by passing both air and steam over heated coal, and consisting of a mixture of carbon monoxide, hydrogen and nitrogen; as well as the waste gases formed in many

industrial processes, are now largely used for the production of power. By adopting such methods of fuel economy to a greater and greater extent, and by recovering in all cases the by-products (ammonia and tar), produced from the twenty million tons of coal annually distilled in Great Britain for the production of the coke required in metallurgical processes, savings would be effected which could be estimated only in millions of pounds sterling.

But we can also make use of other combustible materials, other fuels, and so reduce the rate at which our stock of coal is being depleted. Of these fuels, oil ranks first in importance. Not only does petrol, the more volatile portion of crude petroleum, constitute a fuel for which the demand threatens to exceed the supply, but the higher boiling portions of petroleum, which distil over after the kerosene or illuminating oil, form a fuel which can be burned in boilers, and used for raising steam. At present, the world's production of crude petroleum amounts to between fifty million and sixty million tons, and this therefore constitutes a very valuable supplementary source of energy. In recent years the use of oil has greatly increased, and so great is its heat-producing power—it is one and a half times greater even than anthracite—that it would almost seem as if oil were marked out to take the place of coal, and to become the fuel of the future. But alas! even at the present rate of consumption, it is estimated that the world's reserves of oil would last only a hundred years; and there seems, therefore, no hope that the dream of an age of oil succeeding an age of coal, will ever be realised.

In some of the great timber-producing countries, wood

is still used to some extent as a fuel, but on account of its price and low heat-producing power (about half that of ordinary coal), it cannot find general adoption. Moreover, owing to the great demand for timber not only for constructional purposes, but also for use in many manufactures, of which the manufacture of paper may be taken as an example, the world's reserves of timber are becoming greatly depleted; and the need for the preservation of our timber supplies and for the extension of afforestation, is more urgent even than the saving of coal which would be effected by the greater use of wood as fuel.

But there is one other source of heat energy which, we may hope, will prove capable of more abundant use and so postpone for centuries a world-bankruptcy in fuel. Peat occurs in great abundance and widely distributed, and it has been estimated that the amount of combustible matter in the peat deposits already existing, is greater than in all the known coal-fields.[1] But the removal of the large amount of water which peat contains, is a difficulty which lies in the way of the utilisation of this material as a fuel; and when peat is dried in what was formerly the only economically successful way, namely, by natural drying in air, a bulky fuel with only a low calorific value is obtained. The invention, however, of what is called the "wet carbonisation" process, inspires the hope that a way out of the difficulty has already been found. In this process, the wet peat is heated under pressure to a temperature of about 400° F., and the resulting material, which can be dehydrated

[1] The area of peat moors in Europe has been estimated at 140,000,000 acres; and in Ireland alone the available peat has been estimated as equal to 2,500,000,000 tons of coal.

by pressure, is formed into hard briquettes of "peat coal." This material burns readily and has a calorific value not greatly inferior to that of bituminous coal. Or the dehydrated peat can be employed for the manufacture of producer gas which can be used for power purposes, while the valuable by-products ammonia, tar, and acetic acid, can be recovered.

The utilisation of water-power is, as we shall see later (Chap. IX), a matter in which the chemist can play an important part, and we may be sure that future years and future ages will witness the utilisation, to an ever greater extent, of the energy of flowing and falling water in which, at the present time, such enormous amounts of energy are running to waste.

Although the association of energy with chemical change has been made very obvious to us in connection with the process of combustion, it is also found in connection with all chemical changes. Every chemical system, every collection of substances which can spontaneously undergo chemical change, represents a certain amount of potential energy, and the material change which we observe, and which constitutes what we call a chemical reaction, is merely the outward sign of the conversion of so much potential energy into active energy—heat energy, or some other form of energy. Moreover, whenever a chemical change or reaction occurs, the heat which is given out, the so-called heat of reaction, is, for a given weight of the reacting materials and under specified conditions, constant and definite in amount.

But it must not be thought that all chemical change is

accompanied by an *evolution* of heat. In some cases, the initial substances possess less energy than the final products, and the chemical change therefore takes place with *absorption* of heat. Energy, that is to say, must be supplied to the initial substances in order that they may pass into the final products of change. We distinguish, therefore, between *exothermal* reactions or reactions accompanied by evolution of heat, and *endothermal* reactions or reactions accompanied by absorption or taking in of heat energy.

This way of regarding chemical change as being the outward and visible sign of energy change is a very instructive one; for it is clear that if we can make a substance take up energy — if we can, as it were, pump energy into a substance—we can thereby alter the amount of energy of which that substance is the carrier, and so change its nature. This fact is clearly illustrated by the behaviour of the familiar substance, oxygen.

The molecule of oxygen consists of two atoms, but when the gas is subjected to the action of an electric discharge under particular conditions, it takes up or absorbs some of the energy of the discharge and passes into a gas which, on account of its powerful and characteristic smell, received the name of *ozone* (Greek ὄζω, I smell). The material change, the chemical change, which accompanies the absorption of energy, is the addition of a third atom of oxygen to the molecule of that gas, so that the molecule of ozone consists of three atoms of oxygen. Since ozone contains more energy than ordinary oxygen, it is a more active oxidising agent, and for this reason it is sometimes used for the sterilization of drinking water, the ozone

oxidizing and so destroying the bacterial impurities present. Ozone is also used for the purification of air in confined spaces and in underground "tubes," but opinion is divided with regard to the desirability and efficacy of such treatment.

At Niagara Falls, large quantities of ozone are used in the production of vanillin, the sweet-smelling constituent of the vanilla bean pod, by the oxidation of oil of cloves.

In the case of white phosphorus and red phosphorus, and in the case of the three forms of carbon—charcoal, graphite, and diamond—we have further examples of elements existing in different, so-called *allotropic*, forms containing different amounts of energy.

Perhaps the most vivid idea of the large amount of potential energy stored up in substances can be gained from a consideration of the materials known as *explosives*. In the case of the explosives actually in use, the chemical process which occurs is essentially one of very rapid combustion, with production of gaseous substances occupying a volume which, at the temperature of the explosion, is much greater, perhaps 10,000 to 15,000 times as great as that of the explosive itself.

As early as the seventh century, we read, a rapidly burning mixture, known as Greek Fire, which "came flying through the air like a winged long-tailed dragon, about the thickness of an hogshead, with the report of thunder and the velocity of lightning," was used by the inhabitants of Constantinople in their defence of the city against the Saracens. The discovery of the first real explosive, *gunpowder*, is, however, attributed to Roger Bacon in the thirteenth century;

and since that time man has striven to discover new explosives of greater and greater power, to learn how better to utilise and control the transformation of the enormous stores of potential energy contained in explosives, and to make them work for him both in peace and in war. Some idea of the advance which has been made is gained when we compare the artillery used by the English at the battle of Crécy in 1346, when the guns "threw little balls of iron to frighten the horses," with the modern large gun which can hurl a projectile of nearly a ton in weight to a distance of thirty miles.

Gunpowder is a mixture of potassium nitrate or saltpetre, charcoal, and sulphur, and its action as an explosive depends on the rapid combustion of the sulphur and charcoal at the expense of the oxygen contained in the saltpetre; and although great improvements have been made in gunpowder in recent times, these improvements have been of a physical or mechanical and not of a chemical nature. While still largely used in connection with the beneficent operations of mining and also for pyrotechnic displays, gunpowder is no longer employed as a propellant for military or naval purposes. Its use has been given up not only on account of the large volume of smoke produced in the explosion, which, by speedily hiding everything from view prevents the effective use of quickfiring guns, but also because explosives of very much greater power and efficiency have been discovered.

The first great advance in the chemistry of explosives took place with the discovery in 1846 of *gun-cotton* or "nitro-cotton." Cotton consists, essentially, of the chemical substance cellulose, which is, as we have seen (p. 60), a

compound of carbon, hydrogen and oxygen. When this is acted on by a mixture of nitric and sulphuric acids, various compounds of cellulose with nitric acid (nitrates) are formed which are generally known as "nitro-cellulose." Since not only cotton, but also purified wood fibre or wood pulp (p. 80), and other vegetable fibres consist *essentially* of cellulose, it might be thought that such materials could also be used for the manufacture of "nitro-cellulose." And this indeed can be done. But in none of these cases are we really dealing with a chemical substance possessing entirely uniform properties, and the explosive qualities of the "nitro-cellulose" prepared from the cellulose derived from different sources are not identical. Consequently, although the "nitro-cellulose" from wood pulp could be used as the basis of propulsive ammunition, guns which had been designed for use with a "nitro-cotton" propellant would have to be re-adjusted as regards size of explosion chamber and sighting before they could be used with the different ammunition. Hitherto cotton waste has always been employed for the preparation of gun-cotton, and in order to obtain a reliable explosive with uniform properties, great care must be exercised in the preparation and subsequent purification of the gun-cotton as well as in the selection and treatment of the material used.

When ignited, loose gun-cotton burns with great rapidity, but not so rapidly as to constitute an explosion. The molecule of gun-cotton, however, which, as we might say, is almost bursting with energy, is in a very unstable condition, and when subjected to a shock, as, for example, when a little fulminate of mercury is caused to detonate near it, it suddenly decomposes and gives rise to a large

volume of gaseous substances, nitrogen, oxides of carbon, and water vapour. Since these gases are all colourless, and as no solid materials are formed, gun-cotton explodes without smoke.

As an explosive, gun-cotton possesses the very important property that it can be used wet. This wet gun-cotton will not take fire when a light is applied to it, but when subjected to the shock of a fulminate of mercury detonator, it explodes just as readily as when it is dry. Thus, torpedoes and sea-mines are charged with rolls of moist gun-cotton which have been subjected to a high pressure (six tons per square inch) and so compressed into hard blocks.

The explosive or disruptive effect of gun-cotton is very great by reason of the rapidity with which the decomposition of the substance takes place. Thus, whereas a couple of pounds of gunpowder require about a hundredth of a second for complete combustion, the same weight of gun-cotton undergoes decomposition in about one fifty-thousandth part of a second. It is on this fact that the shattering or disruptive effect, the "brisance," depends. It is this fact, also, which makes gun-cotton, which is very valuable as a "high" or "disruptive" explosive, unsuitable for use as a "low" or "propulsive" explosive in guns. It would simply burst the gun.

The difference in the action of a "low" and of a "high" explosive can be illustrated by a well-known experiment. A piece of thin sewing cotton is attached to a fairly heavy weight suspended so that it can swing freely. If the thread be now pulled very gently, the weight can be caused to assume a vigorous motion. This corresponds with the

action of a "low" explosive, in which the explosion takes place relatively slowly. If, on the other hand, a sharp sudden pull be given, the thread snaps. This corresponds with the action of a "high" explosive.

Although gun-cotton cannot be employed as a propellant, the advantages attaching to a smokeless explosive are so obvious, that attempts were made to overcome the difficulties due to the rapid rate of explosion. These attempts to "tame" the gun-cotton, have been entirely successful. Nitro-cotton dissolves in various liquids, such as acetone or a mixture of alcohol and ether, and when these solvents are evaporated off, the nitro-cotton is obtained as a gelatin-like material, which is familiar to everyone under the name of collodion. In this gelatinised material the disruptive properties of the gun-cotton are greatly modified. Such gelatinised gun-cotton was the first smokeless powder to be used.

A further advance in the chemistry of explosives was made by the Swedish chemist, Alfred Nobel. When glycerine, which, as we have seen (p. 34), is readily obtained from animal or vegetable fats and oils, is treated with a mixture of nitric and sulphuric acids, it behaves similarly to cotton and yields a substance "nitro-glycerine," which is a liquid and very powerful explosive. This substance, discovered by Nobel, was difficult to handle on account of its great sensitiveness to shock, and was the cause of many fatal accidents; but it was found that if the liquid nitro-glycerine was mixed with kieselguhr, a fine earth composed of the siliceous skeletons of marine diatoms, the explosive could be transported and handled with comparative freedom from

danger.[1] In this form nitro-glycerine has been largely used under the name of *dynamite*, its explosion being brought about by means of a fulminate of mercury detonator.

When nitro-cotton is added to nitro-glycerine a tough jelly-like mass is formed known as *blasting gelatin*. That this explosive is more powerful than dynamite, that it is, indeed, one of the most powerful blasting explosives known, will cause no wonder, since the nitro-glycerine is not mixed with an inactive material like kieselguhr, but with a substance which is itself an explosive.

The British service powder, *cordite*, is prepared by mixing a "paste" of gun-cotton (65 per cent.) and nitro-glycerine (30 per cent.), with acetone, and adding a quantity of vaseline (5 per cent.). The mixture is then forced by hydraulic pressure through a die into the form of a thread or cord. Hence the name cordite. After evaporating off the acetone, the cordite forms a horn-like material which is very insensitive to shock and safe to handle. This "taming" action of gelatinisation on two of the most powerful explosives, is one of the most important and remarkable discoveries in this branch of science; and nitro-cotton, gelatinised in one way or another, is now the basis of all propulsive ammunition.

Although nitro-cotton or gun-cotton is extensively employed as a high explosive, more especially in torpedoes, for use in shells other explosives derived from the products of distillation of coal are employed. Of these explosives the two most important and most used are *picric acid* and *trinitrotoluene*.

[1] Wood-flour or wood-meal, burnt cork, charcoal and other materials are also used as absorbents in place of kieselguhr.

When carbolic acid or phenol, to give it its scientific name, is treated with a mixture of nitric and sulphuric acids, there is formed trinitrophenol or picric acid. As ordinarily obtained, it is a faintly yellow crystalline substance, which has long been used as a yellow dye for silk. It melts to a liquid at a temperature of 252° F., and in this state it is run into the shell. On account of the honey-yellow colour of the molten picric acid, this substance received from the French the name of melinite; while in this country it is called lyddite, on account of the fact that it was at Lydd, in Kent, that its use as a high explosive was first tested. In other countries it receives still other names, such as pertite, ecrasite, and shimose. Although picric acid can be handled with perfect safety, its destructive power, when exploded by means of a suitable detonator, exceeds that of gun-cotton or dynamite. Some idea of the enormous amount of potential energy contained in picric acid can be gained from the fact that when a pound of the substance is exploded, it liberates an amount of energy equal to that required to raise a weight of over a ton more than one hundred yards into the air. Unfortunately picric acid has the property of forming with metals compounds which are much more sensitive than itself, and so may give rise to untoward accidents. Another explosive, therefore, has come into favour in recent years, a substance derived from the hydrocarbon toluene, and called trinitrotoluene, or T.N.T. This substance also is a solid, and can be subjected with impunity to very rough usage; a bullet, even, may be fired into the mass without producing any effect. When detonated, however, trinitrotoluene explodes with a violence not much inferior to picric acid, but as the oxidation of the carbon in

the compound is by no means complete, dense black clouds of carbonaceous matter are produced, and this has led to the nicknames of "Coal boxes" and "Jack Johnsons" being applied to the shells filled with this explosive. For use as a high explosive, trinitrotoluene is also frequently mixed with ammonium nitrate.

But it is not merely for the purpose of strengthening man's arm in war that explosives have found an application; they have also, by rendering possible such great engineering works as the Suez Canal and the Panama Canal and the boring of tunnels through the mountains of the earth, through their use in mining, and in many other ways, played an important part in the peaceful progress of civilisation. Even in the piping times of peace, high explosives are produced, in the United Kingdom alone, and chiefly at Nobel's factory at Ardeer in Ayrshire, the largest explosives factory in the world, to the amount of 17,000 to 18,000 tons per annum. Enormous as is now the power wielded by man by means of these explosives, it may confidently be anticipated that chemistry will yet give him control of still more concentrated forms of energy, and will put into his hands still more powerful weapons for the advance of civilisation—or, if he will, for its destruction.

CHAPTER V

CELLULOSE AND CELLULOSE PRODUCTS

WE have seen in the previous chapter how the woody material of plants has, by the age-long action of natural forces, become converted into the most valuable of all fuels, coal; and we have also seen how cotton can, by the action of nitric acid, be transformed into one of the most powerful of explosives. We must now consider very briefly how the chemist has, in other ways, succeeded in changing the aspect and nature of the cellulose, of which cotton and wood fibre essentially consist, so as to produce other materials which can be fashioned into articles of utility and of beauty, which minister to the wants, the comfort, and even the luxury of man.

The chemical substance cellulose belongs to a group of compounds consisting of carbon, hydrogen, and oxygen, in which the hydrogen and oxygen are present in the proportion of two atoms of the former to one of the latter. Since this is the proportion in which these two elements combine to form water, it was thought that cellulose and the other compounds belonging to that group, were compounds of carbon with water, and so the name *carbohydrate* was applied to them. The different sugars, such as grape sugar, fruit sugar, cane sugar, and also starch and a number of other substances, belong to the

class of the carbohydrates. In cellulose the carbon, hydrogen and oxygen are united in the proportions of six atoms of carbon, ten atoms of hydrogen, and five atoms of oxygen ($C_6H_{10}O_5$), although we do not know how many atoms of carbon, hydrogen and oxygen are really contained in the molecule. We therefore represent cellulose by the formula $(C_6H_{10}O_5)_n$ where n is an unknown whole number.

The purest naturally occurring form of cellulose is cotton, the hairy material which covers the seeds of various species of the cotton plant (*Gossypium*). When this has been chemically treated with alkalies and bleaching agents, and with acids, in order to remove various organic and mineral impurities, the product constitutes what is called cellulose. This is one of the most important and valuable substances in present-day civilisation, being employed in the manufacture not only of cotton and linen textile materials, but also of explosives, of paper, and of other substances to some of which we shall refer below. Its great value for the manufacture of paper depends mainly on the fibrous character of naturally occurring cellulose, and also on the fact that it is a very stable substance and is not acted on by the atmosphere nor by most of the other substances with which it ordinarily comes into contact.

Less than a hundred years ago, when the production of paper was hampered by a Government duty, and before a penny postage had stimulated the growth of private and business correspondence, or education had created the present demand for cheap newspapers and cheap books, paper was manufactured entirely from cotton and linen

rags. But nowadays the supply of these is quite inadequate to meet the demand, and recourse is had to the less pure forms of cellulose which constitute the skeletal frame-work of all vegetable structures; and large quantities of more or less pure cellulose are produced at the present day, from straw, various grasses (especially esparto grass), and from wood, for use in the different industries of which cellulose is the basis.

Of these different sources of cellulose, wood constitutes by far the most important. Wood fibre consists mainly of a compound of cellulose with lignone, encrusted frequently with resinous matter, and in order to isolate the cellulose, this compound must be decomposed. Formerly this was done by boiling the wood, in the form of shavings or chips, with caustic soda (giving rise to "soda pulp"), but the latter substance has now been very largely replaced by calcium bisulphite (or acid sulphite of lime),[1] the wood being boiled with the liquor under a pressure of several atmospheres. Not only is the wood fibre thereby chemically broken up with production of cellulose, but the latter is also bleached to some extent by the sulphite. The cellulose is now separated from the sulphite liquor, washed and beaten with water so as to break down the fibres into small shreds, in which form it constitutes *wood pulp* ("sulphite pulp"). A solution of sulphate of soda is also employed to a certain extent for the disintegration of the wood-fibre and the production of cellulose, the pulp so obtained being known as "sulphate pulp."

[1] This substance is formed by the action of sulphurous acid (solution of sulphur dioxide in water) on limestone.

Pulp is produced, however, not only by chemical but also by mechanical means, the wood being ground to powder on rapidly revolving, wet grindstones. In this "mechanical pulp," however, the cellulose has not been separated from the lignone and the resins in the wood; it is not of a strictly fibrous nature and does not felt together readily. It is suitable, however, for mixing with other paper-making, fibrous material, especially cotton.

Of the paper manufactured in Great Britain, by far the largest proportion is made from wood pulp.

For the manufacture of paper, the fine cellulose fibres obtained from the disintegrated cotton rags, grass, or wood pulp, are bleached, washed, and mixed with colouring matters if desired. They are then suspended in water and run over an endless band of wire gauze, through which the water drains away, and the fibres are caused to felt together by giving a vibratory motion to the band of gauze. The web of felted pulp is now carried between heated rollers whereby the paper is dried.

The paper so obtained is loose in texture and of the nature of blotting paper; and to make it suitable for writing or printing it must be sized. For this purpose it is passed through solutions of alum and of rosin soap (p. 156), whereby a compound of rosin and aluminium is formed which binds the fibres together and prevents the ink from running. The addition of the sizing materials may also be made to the pulp before making into paper. Sometimes, also, powdered gypsum, white clay, or similar substances are added to the paper pulp in order to "load" or give body to the paper, fill up its pores, and allow of a more

highly glazed surface being obtained by calendering, or rolling with hot rollers.

By immersing paper for a short time in a fairly concentrated solution of sulphuric acid, the cellulose is converted into a gelatinous mass which fills up the pores of the paper, and on being thoroughly washed, the paper is found to be parchmentised, or converted into a non-porous material resembling parchment (prepared skin of the sheep or she-goat). Such *parchment paper* can also be prepared by immersing paper in a solution of zinc chloride; and by compressing together a number of sheets of such parchment paper, the compressed fibre, or "hard fibre," so largely used in the manufacture of travelling cases and trunks and as an insulating material for electricity, is obtained.

When one adds ammonia to a solution of bluestone or copper sulphate, a pale blue solid, copper hydroxide, is formed; and if this solid is dissolved in ammonia, a clear deep blue coloured liquid (a solution of cuprammonium hydroxide) is produced. This liquid has the important property that it can dissolve cellulose, and by coating paper with the solution obtained and then immersing it in acid, the cellulose is thrown out of solution as a gelatinous mass which coats the paper and renders it waterproof. In this way *Willesden paper* is prepared.

As far back as 1889, there was exhibited in Paris a material which, in its general appearance, imitated in a remarkable manner the fibre spun from the glands of the silkworm. This material, however, invented by the French chemist Count Hilaire de Chardonnet, was not silk, nor was it derived from any animal source whatever, but from

the vegetable material cellulose.[1] Nitro-cellulose, or nitro-cotton, as we have seen, can be dissolved in certain liquids, such as a mixture of alcohol and ether, and when the somewhat viscous liquid which is thus obtained is squirted through fine openings, and the jet of liquid allowed to pass through water, thin threads or filaments are obtained. By treating these threads with certain solutions, *e.g.* a solution of sulphide of ammonium, the "nitro-groups," (NO_2), to the presence of which the gun-cotton owes its explosive properties, are removed, and there is again obtained what is practically cellulose, the natural structure of which has, however, been destroyed by the treatment to which it has been subjected. The threads and fibres so produced have all the superficial appearance and lustre of silk, and it was by this process that the fibre produced by the silkworm was first imitated and counterfeited in a commercially successful manner.

But it was not long before other and better methods of transforming cellulose into fibres and threads resembling silk were invented. We have already seen that cellulose dissolves in a solution of blue cuprammonium hydroxide, and when the viscous mass which is thus obtained is squirted into a suitable hardening liquid, threads of a silk-like lustre are obtained.

The method, however, by which most of the artificial or imitation silk is made at the present day, the so-called viscose process, was invented by two English chemists, C. F. Cross and E. J. Bevan. As the basis of this process there is used wood pulp, prepared by the maceration and

[1] True silk belongs to a class of substances known as proteins, and contains nitrogen as well as carbon, hydrogen and oxygen.

chemical treatment of wood. This pulp is treated with a solution of caustic soda and then with the liquid called carbon disulphide, whereby a thick syrup-like mass is obtained. By forcing this viscous material through minute apertures into a suitable liquid, silky filaments are produced which can be spun into threads suitable for knitting or weaving. The artificial silk, the transformed and transfigured wood fibre, obtained by this process is superior in lustre, in strength, and in the uniformity with which it can be dyed, to that obtained by the processes previously described. Although more lustrous than silk and costing only half the price, artificial silk has not been found to enter into direct competition with the natural product; but for use in the production of articles of apparel, whether woven or knitted, of embroideries and laces, imitation furs and tapestries, it has developed for itself and by reason of its own distinctive properties, a field of usefulness already great and rapidly expanding. At the present day the world's production of artificial silk is estimated at about 7000 tons. And when we admire the beauty of this material, do not let us altogether withhold our appreciation of the work of the chemists by whose ability the woody fibre of the tree has been increased in value not merely a hundred but almost even a thousand-fold.

When the syrup-like viscose is kept for some days it undergoes spontaneous decomposition with production of a hard horn-like material which may for many purposes replace the material celluloid. Transparent and non-inflammable films can also be obtained by spreading viscose on glass at a temperature of about 175° F.

The artificial silk to which we have just referred, must not be confused with the lustrous material known as mercerised cotton, so called after the discoverer of the process, John Mercer. Cotton, in its natural state, consists of flat, twisted fibres, but when these fibres, tightly stretched, are immersed in a solution of caustic soda or soda lye, the fibres swell up, become untwisted, and assume a nearly straight, rod-like form. The surface of these fibres is covered with a number of smooth ridges which, reflecting the light falling on them at different angles, give rise to a lustrous appearance or sheen.

To one more application of cellulose, familiar to all, a brief reference must be made. In 1869 it was found that if camphor is added to a mixture of nitro-cotton and alcohol, a hard, horn-like material is obtained, which can readily be fashioned, while hot, into articles of various shapes and form. This material has received the name of xylonite or celluloid, the trade-mark name by which it is registered in the United States, the country in which it is chiefly manufactured. Although naturally of a clear gelatin-like appearance, celluloid can easily be dyed of various colours, can be rendered opaque by the addition of different substances, and can, by special treatment, be made to imitate not only such materials as bone and ivory, but also tortoise-shell, marble, and agate. Light in weight and not readily breakable, celluloid is used in imitating amber, and for the manufacture of photographic films, combs, knife-handles, soap-boxes, and other articles of common use too numerous to mention. But it is a material the use of which is not altogether free from danger.

The basis of celluloid, we must remember, is a form of gun-cotton, and although the more violent activities of the latter are considerably subdued by the camphor and other substances with which it is mixed, the material is, nevertheless, very readily inflammable and has, in consequence, given rise to many disastrous conflagrations. To start the combustion of the celluloid, it is not necessary to bring it into contact with a naked flame. Contact for a short time with an incandescent electric light bulb may be sufficient to start the combustion, and fires have even been caused by the accidental focussing of the sun's rays on articles of celluloid exhibited in shop windows.

Although the dangerous inflammability of celluloid can be reduced by the addition of various salts, dextrin, and similar substances, the discovery of a material having the many good qualities of celluloid, but free from the dangers attending its ready inflammability, is clearly one of great importance. The acetate of cellulose, known commercially as cellite, when mixed with camphor or suitable substitutes, yields a material called *cellon* or sicoid (as it is called in France), which resembles, and is even superior to, celluloid in its general properties, and is not inflammable. It is more elastic than celluloid and is used as a substitute for guttapercha, vulcanite, etc. It is used for making the bristles of hair brushes, for the production of the imitation horse-hair of which ladies' hats are frequently made, and for the manufacture of cinematograph films. In the form of a thick viscous solution it is employed as a flexible varnish for wood, paper, and metal, for enamelling aeroplanes, and as an insulating covering for electrical conductors.

But we have not yet exhausted the uses to which the most valuable substance cellulose can be put through the ingenuity of the chemist. If instead of mixing the nitro-cellulose with camphor so as to produce celluloid, it is mixed with a drying oil, like linseed oil, and with colouring matters, and is then spread on a fabric, a sort of "oil-cloth" is obtained; and on passing this between suitably cut rollers, the material is grained and a very good imitation leather is produced. Such imitation leathers, like Rexine for example, are now very largely used for the upholstering of furniture and for other purposes.

CHAPTER VI

VELOCITY OF REACTIONS AND CATALYSIS

THE overthrow of the phlogiston theory by Lavoisier towards the end of the eighteenth, and the enunciation of the atomic theory by Dalton early in the nineteenth century, mark the beginning of a new era in chemical science, when the activities of chemists were directed in an increasing degree to the preparation and quantitative determination of the composition of new substances and naturally occurring materials, as well also as to the determination of the atomic weights of the elements. Moreover, the study of the compounds of carbon, a branch of science to which the name of Organic Chemistry is applied, began to be developed with an ever-increasing energy; and in this domain, the problems connected with the constitution of the molecule, that is, with the arrangement of the atoms within the molecule, were so important for the proper understanding of the enormous array of substances which chemists were able to prepare, that such questions exercised, and very properly exercised, a powerful fascination over the workers in that branch of chemistry. The quite wonderful results which were thereby obtained had their value, also, not merely in the domain of theoretical chemistry, but led to some of the most brilliant achievements of practical chemical science—to the preparation of dyes, drugs, perfumes, and many

other materials of the greatest industrial and, one may say, human value—so that one need not hesitate to regard such work as amongst the most important in the whole history of the science. By the workers who achieved such splendid successes, chemical reactions were regarded entirely or mainly from the materialistic point of view, from the point of view of the substances undergoing change and of the substances produced by the change. But there is clearly another aspect of the subject which demands attention. Just as we have already recognised that substances are carriers of energy, and that a chemical reaction or chemical change is a mode of transforming chemical energy into other forms of energy, so also in modern chemistry, one is concerned not merely with the material *products* of chemical change, but also with the *process* of chemical change itself. Why does a chemical reaction take place, and what are the laws governing the rate at which and the extent to which a chemical reaction proceeds? These are the questions which chemical dynamics, one of the most important branches of modern chemistry, seeks to answer.

Although it is not possible to discuss the subject fully here, the attempt must be made to give some indication of the more general principles in order that we may gain a better appreciation of present-day chemistry and a more intelligent understanding of some of the most recent and economically most important industrial processes, the development and success of which depend on dynamical investigations.

When, in the thirteenth century, the great Dominican monk and Bishop of Regensburg, Albertus Magnus—*magnus in magia naturali, maior in philosophia, maximus in*

theologia—used the word "affinitas," he merely summed up the views current at that time, that chemical reaction is due to a similarity or kinship between the reacting substances. But although this term affinity or chemical affinity is still in use, it must now be regarded not as signifying any natural resemblance or family relationship, but rather as a force, of the nature of which we have as yet no certain knowledge, which acts between different kinds of matter and which, under certain conditions, brings about a chemical action between them. The existence of this force is postulated in order to account for the fact that chemical change or reaction will take place between substances when thereby potential energy can be converted into work.

One of the most important factors in the process of chemical change is the speed with which it takes place, the velocity of the reaction. That there is a great variation in the rate at which chemical change takes place is so obvious as almost to render its emphasis unnecessary. The rusting of iron, the oxidation of aluminium, the burning of wood, the explosion of gun-cotton, are chemical changes which take place with markedly different velocities. This great difference in the rate of reaction we shall be inclined to attribute to differences in the chemical affinity, and in so doing we shall be right, but only partly right; for when one studies the process of chemical change more fully, it is found that the rate of a reaction does not depend merely on chemical affinity, but also on a number of other factors. Of these factors, one of the most important is the *concentration* of the reacting substances, that is, the amount of the substances in a given volume. We shall be able to understand this more readily, if we fix

our attention, for the present, on reactions between gaseous substances. When a substance is in the state of a gas, its molecules are supposed, according to the kinetic theory of matter, to be moving about with great velocity in all directions, and combination or reaction between two substances, A and B, can take place only when molecules of A and B collide or come within each other's sphere of influence. If, then, we have a certain number of molecules of the substance A and a certain number of molecules of B moving about in a given space, an A molecule will collide with a B molecule a certain number of times per second, and the rate of reaction, therefore, will have a certain value. But suppose that the number of B molecules is now doubled. It is clear that in the same unit of time, an A molecule will now have double the number of chances of colliding with a B molecule and of entering into reaction with it, and the rate of reaction will therefore be doubled. Similarly, if we double not only the concentration of the B molecules, but also that of the A molecules, then it is clear that the rate of reaction will again be doubled; that is, the reaction now takes place four times as fast as it would have done with the original concentrations of the two substances. The speed of a reaction, in fact, is proportional to the product of concentrations of the reacting substances. This law of the dependence of the speed of a chemical change on the concentrations of the reacting substances, was discovered by two Norwegian scientists, Guldberg and Waage, and is generally known as the law of mass action.

But the velocity of chemical change is also very greatly influenced by the temperature, a fact to which we have

already alluded in Chapter II. Although the speed of different reactions is affected in a different degree by temperature, we can take it as a convenient approximation that the speed of a reaction is doubled by raising the temperature 18° F. A simple calculation will show what the magnitude of this effect may be. Suppose that a reaction requires one second for its completion at the freezing-point of water, that is at 32° F. At 212° F., the boiling-point of water, the same change would take place in about one-thousandth of a second; and if we raise the temperature but a little more, say to 400°, the time required for the change will now be only about one-millionth of a second. On the other hand, a change which would require one second to take place at 400°, would need, at 32°, a period of a million seconds, that is, about eleven and a half days. This influence of temperature is of the greatest importance, and on its recognition may depend the success of an industrial process.

But there is another important result which has followed from the dynamical study of chemical reactions, the recognition, namely, of the fact that chemical changes are reversible, and that the direction in which reaction between different substances takes place depends not merely on chemical affinity but on the relative concentrations of the different substances. When steam (oxide of hydrogen) is passed over heated iron, oxide of iron and hydrogen are produced. On the other hand, when hydrogen is passed over heated oxide of iron, steam (oxide of hydrogen) and metallic iron are formed.

$$\left\{\begin{matrix}\text{Iron} \\ \text{Oxide of hydrogen}\end{matrix}\right. \rightleftarrows \left.\begin{matrix}\text{Iron oxide} \\ \text{Hydrogen}\end{matrix}\right\}$$

In the former case, the steam is present in large abundance whereas the hydrogen which is formed is swept away and cannot, therefore, react with the oxide of iron. In the latter case, the hydrogen is present in abundance, while the water vapour is carried away in the stream of gas and so is prevented from reacting with the metallic iron. By altering the relative concentrations of the steam and the hydrogen, therefore, we can cause reaction to take place in whichever direction we please. But let us now arrange matters so as to prevent the removal of the hydrogen or of the steam, by heating the substances together in a closed vessel, then we shall find that both reactions will take place; steam will react with iron, and hydrogen will react with oxide of iron, so that finally a state of balance or equilibrium will be produced, at which there will be a certain definite relationship between the concentration of the steam and the concentration of the hydrogen.

So long as the temperature is kept constant, the same state of balance or equilibrium will be reached, no matter what may be the initial amounts of hydrogen and of steam, but if the temperature is altered, the state of equilibrium will also be altered. By raising or lowering the temperature the one or the other reaction can be caused to take place to a greater and greater extent, and the direction in which the equilibrium is thereby altered is found to be intimately associated with the heat effects which accompany the chemical change.[1]

[1] The law which is found to obtain here can be stated in a simple form. It will be clear that if one reaction is accompanied by an evolution of heat, then the reverse reaction must be accompanied by an absorption of heat. *When the temperature is raised, the latter reaction, the reaction accompanied by absorption of heat, is favoured, whereas lowering the temperature favours the reaction*

The discovery of the laws of chemical change, and the recognition that, theoretically at least, all reactions are reversible, mark one of the most important advances in our knowledge of chemical processes and of the action of chemical affinity. Some of the consequences which flow from this will be discussed in the sequel.

Although, as we have said, the progress of a chemical reaction and the rate at which a chemical change proceeds, are influenced both by the concentration of the substances and by the temperature, it is found that the velocity of a chemical reaction may also be profoundly affected in another way which, on account of its very great importance both in the laboratory and in the factory, demands a fuller consideration.

In the early decades of last century, a number of phenomena were observed which, although isolated and apparently unconnected, all possessed one common characteristic, namely that of a reaction the speed of which was markedly increased by the addition of certain substances in minute, sometimes in almost infinitely minute amount. Owing to such additions, it was found, substances which seemed, under the particular conditions, to be without action on each other, reacted with appreciable, sometimes even with great readiness. From the magnitude of the result produced, it was evident that the foreign substance could not enter into the reaction in the ordinary way; but, as the Swedish chemist, Berzelius, pointed out, the substance which was added appeared to act merely by

which takes place with evolution of heat. Only when no heat effect accompanies chemical change is the equilibrium unaffected by change of temperature.

its presence and by "arousing the slumbering affinities of the substances," and so allowing them to react. How these slumbering affinities were aroused, Berzelius did not hazard a guess, but in order to give a name under which such phenomena could be classed, he introduced the term "catalysis" (a word which signifies a loosening); and a substance which brings about catalysis is called a "catalytic agent" or a "catalyst." For long the phenomenon of catalysis, of which the number of cases observed rapidly increased during the nineteenth century, was regarded by chemists as Gulliver was regarded by the learned men of Brobdingnag, as a *lusus naturæ;* it was relegated to the realm of the mysterious, and chemists became only too prone to think that the label of catalysis was at the same time an explanation of the phenomenon. It was, indeed, only towards the end of last century and owing to the development of the experimental methods of measuring the rate of chemical change, that the phenomenon of catalysis and the behaviour of catalysts began to form the subject of systematic investigation. During the past thirty years, the energy of many workers has been directed along this line of investigation, and much valuable information has been accumulated regarding the main characteristics of catalysis and the behaviour of different catalysts. With some of these we must now become acquainted.

As we have already indicated, one of the most striking features of catalysis is the magnitude of the effect produced, compared with the small amount of the substance producing it. An excellent illustration of this is seen in the influence which moisture exercises on the rate of combination of gaseous substances. When hydrogen and

oxygen, the two gaseous substances by whose combination water is formed, are heated together, they combine, and if the temperature is sufficiently high, say about 1100° F., the combination takes place with explosive violence. But this occurs only when a trace of moisture is present in the gases. If the last traces of moisture are removed from the gases by allowing them to remain for more than a week in contact with the substance known as phosphorus pentoxide (obtained by burning phosphorus in air), which combines with the greatest avidity with water, the mixture of hydrogen and oxygen can then be heated even to a temperature of nearly 1800° F. without explosion occurring. Not only in the case of hydrogen and oxygen, but in the case also of many other gases, combination is found to depend on the presence of moisture, of which, however, the merest trace suffices.

This action of moisture, and, indeed, the action of catalysts generally, has been likened to the action of oil in the bearings of a machine; a catalyst diminishes, as it were, the hindrances to change of whatever nature these may be without itself being used up in the process.

No less interesting or important is the extraordinary influence exerted by many solid substances on the rate at which combination between gases takes place. Thus, if we again consider the case of hydrogen and oxygen, it is found that although combination of the two gases takes place at high temperatures with great and explosive velocity, at the ordinary temperature no trace of combination can be detected. In fact, from the influence which temperature has been found to exercise on the

rate of combination, it has been estimated that no appreciable amount of combination would occur at the ordinary temperature even in a period of a billion years. But if a little metallic platinum be brought into contact with the mixture of the two gases, combination proceeds with appreciable velocity; indeed, if the platinum is used in a finely divided form, known as platinum sponge or platinum black, the rate of combination may be so great that an explosion results. This action of platinum, one of the first cases of catalytic action to be observed, brings out very clearly two of the main characteristics of the phenomenon, namely, the great change produced in the speed of the reaction, and the fact that the catalyst remains unchanged in amount. The same piece of platinum can be used to bring about the combination of unlimited quantities of hydrogen and oxygen.

This remarkable behaviour of finely divided platinum which greatly impressed, as well it might, the minds of the early observers, was not long in receiving a practical application. In 1823 it was observed by Döbereiner that if a jet of hydrogen was allowed to impinge on a piece of spongy platinum exposed to the air, the heat of combustion of the hydrogen raised the platinum to incandescence, and the hydrogen became ignited. Döbereiner constructed an apparatus in which hydrogen was produced by the action of sulphuric acid on zinc; and when a tap was opened the gas escaped in a fine jet which impinged on a piece of spongy platinum. In this way fire could be obtained, and, as a matter of fact, this Döbereiner lamp was largely used for that purpose before the days of matches.

Although platinum is by no means an universal catalyst for all reactions—no such universal catalyst is known—it has nevertheless been found that platinum acts very generally as a catalytic accelerator of oxidation reactions, or reactions in which gaseous oxygen takes part. Oxide of cerium, which forms a small part of the Welsbach incandescent gas mantle, also acts as a catalyst and accelerates the combustion of the coal-gas.

The attempt made in recent years to apply spongy platinum for the purpose of automatically lighting a jet of coal-gas did not meet with success, by reason of the fact that after a time the platinum was found to lose its effectiveness. This destruction of the catalytic activity, this "poisoning" of the catalyst, as it has been called, is a phenomenon of the greatest importance, the recognition of which has been, as we shall learn more fully presently, not only of purely scientific interest, but also of the greatest industrial importance.

The acceleration of the combustion of hydrogen by platinum can be regarded as a particular case of "surface action," the reacting gases, hydrogen and oxygen, being "condensed" on the surface of the platinum and so brought into more intimate contact. But all solids, and not merely platinum, exhibit this surface action and accelerate the combustion of gases at temperatures below their ignition point, although with an efficiency which varies greatly with the nature of the substance and the fineness of its subdivision. The difference between the catalytic activity of the different substances tends, however, to disappear as the temperature is raised, and when the solid substances are raised to incandescence they are all found to possess the

property of accelerating gaseous combustion in about the same degree. This fact has recently received, in this country and in America, important applications in the process known as "surface combustion."

If a mixture of, say, coal-gas and air is forced through the walls of a porous tube of fire-resisting material, and the issuing gas is ignited, combustion takes place, without flame, in the surface layers of the tube which is soon raised to incandescence and becomes a powerful radiator of heat; or, one may pass the gas mixture through a mass of small granules of refractory material—fireclay, alundum (oxide of aluminium), etc.—forming for example the hearth of the furnace, and so obtain "surface combustion" on each granule (Fig. 8). By these means the efficiency of gaseous heating, either for industrial or for domestic purposes, can be greatly increased.

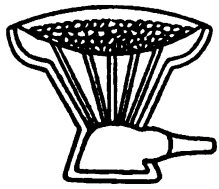


FIG. 8.—SURFACE COMBUSTION GAS COOKER.

The gas, passing up through the narrow channels in the body of the cooker, burns on the surface of the granules of refractory material, which are thereby raised to incandescence and radiate heat.

We have already seen (p. 19) that when a burning gas is cooled to below its ignition temperature, it is extinguished. And so, when using a gas flame to heat a cold object, the flame in contact with the object to be heated is extinguished, and heating takes place only by radiation from the hot gas. By means of "surface combustion," however, the whole of the combustible gas can be burned and its heat value therefore completely utilised, while the radiation from the incandescent solid surface is greatly superior to that from the gas. With the increased

use of gas for heating purposes, the surface combustion process promises, therefore, to be of the highest importance in increasing the efficiency and diminishing the cost of heating.

By chemists the importance of catalysis is now fully recognised, and the systematic search for the most suitable and effective catalyst for a given reaction, is a well-established part of chemical investigation. But it is part of the romance of science that discoveries of value are made not only as the result of consciously directed effort, but also by the aid of "that power which erring men call Chance." And in this connection the following tale may be re-told, for it illustrates not only the special action of a catalyst, but also the important *rôle* which catalysis may play in industry.

For the preparation of a certain dye—it was a dye called sky-blue alizarin, but the name does not matter—the necessary ingredients were heated for some time in a vessel made of iron. But in the course of time fresh apparatus had to be installed; and with this apparatus no sky-blue alizarin was obtained, but something entirely different. What could be the reason of the failure? The process was carried out in the same way as before, and the workmen were the same, or were under the same direction. The apparatus, certainly, was new, but it was exactly the same as the old apparatus. And yet, no; it was not exactly the same. The new apparatus, instead of being entirely of iron, had a copper lid. But surely that could not be the cause of the different behaviour. Yet so it was, for the small trace of copper derived from the lid exerted it was found, a powerful catalytic influence on the course of

the reaction, and instead of the substances reacting so as to form sky-blue alizarin, a further reaction took place which gave rise to a totally different substance.

It might perhaps seem as if the tracing of the trouble to its source would finish the story, but this is by no means the case. Accident had thrown a catalyst for a new reaction in the way of the chemist, who, by careful investigation, found that a trace of copper enabled the ingredients used, as well as a number of other similar substances, to react in a particular manner, and in this way *a new and important series of dyes was discovered.* It all seems very simple; all a matter of "happy accident." But was it by a happy accident that the cause of the trouble in the first instance was discovered? Or was it a happy accident that converted a source of trouble in one process into a source of gain in another? How would the matter have stood without the trained intelligence of the chemist with his knowledge of the importance of little things, with his trained faculty of observation and his ability to make use of the facts which he observed?

In astronomy one deals with magnitudes so vast as to be beyond the grasp of our minds; in the domain of catalysis the magnitudes are, in some cases, so small that it becomes almost equally impossible to form a true conception of them. But in order that the reader may have some knowledge of the very minute amounts of substance which will yet suffice to affect appreciably the speed of a reaction, let me give one example out of the many which might be chosen. When one dissolves sulphite of soda in water, the oxygen of the air slowly oxidises the sulphite of soda to sulphate of soda. By the addition of certain

use of gas for heating purposes, the surface combustion process promises, therefore, to be of the highest importance in increasing the efficiency and diminishing the cost of heating.

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In astronomy, the [illegible] be beyond the [illegible] catalysis the [illegible] it becomes [illegible] ception of them. [illegible] some knowledge of the [illegible] which will yet [illegible] reaction, let [illegible] might be [illegible] water, the [illegible] of soda [illegible]

catalysts, the speed with which this process takes place can be greatly increased, and in this connection copper has been found to be very efficient. In fact, if only one grain of blue-stone or copper sulphate is dissolved in 1,400,000 gallons of water, or one grain in about 250,000 cubic feet of water, the presence of the copper can be detected by its action in accelerating the oxidation of the sulphite of soda! But we are so accustomed to judge of the importance of a thing by the amount of space it occupies, that in asking the reader to recognise the infinite importance of the infinitely small, and to accept the illustration I have given, sober fact of science as it is, I am almost afraid that I shall be considered as putting too great a strain on his credulity.

But, indeed, we need not go far in order to have impressed upon us the importance of these catalytic actions. The human organism itself is like a laboratory in which numerous reactions and marvellous transformations take place unceasingly; the transformation of the food consumed into the bone, and flesh, and blood of the body, and the slow combustion of the tissues to yield the energy and heat necessary for vital activity. And so it is also with the vegetable organism in which we have the building up or *synthesis*, not only of the complex materials which serve as foodstuffs for the animal creation, but also of those sweet-smelling essences and the compounds which give to flowers their varied odours and colours. Many of these substances, the products of Nature's laboratory, can also be made in the laboratory of the chemist, and their synthesis from simple inorganic materials constitutes the crowning achievement of chemical science. But how different are

the methods of the chemist from those of Nature. In his laboratory the chemist makes use of high temperatures and the action of powerful and corrosive reagents; but in the laboratory of Nature, the building up of even the most complex compounds takes place quietly and smoothly at the ordinary temperature. All this the animal or vegetable organism accomplishes by utilising appropriate catalysts, accelerators of reactions, the so-called enzymes, which are themselves produced within the living cell of the plant or animal. The ptyalin of the saliva, the pepsin of the gastric juice, the trypsin of the pancreas, the diastase of the sprouting barley-corn, the zymase of the yeast, which has from time immemorial been used by man for the conversion of sugars into alcohol—these are some of the numerous catalytic agents which Nature produces and of which she makes use in her marvellous achievements in chemical synthesis.

But substances exist which can destroy the efficiency of these catalysts, and thereby retard the life processes in the plant or animal. These substances we call poisons. And it is a noteworthy fact that this behaviour, so familiar in the case of living organisms, has its analogy, as has been pointed out, in the case of non-living catalysts. The recognition of this fact has proved to be of the greatest importance in the application of catalysis to industrial processes.

In the manufacturing industries it may truly be said that time is money; and to produce an article of manufacture at a more rapid rate is the same as saving time. And this is just exactly what a catalyst enables one to do. It is, therefore, not surprising that in almost all branches

of chemical industry the value of catalysts has become increasingly recognised. By their introduction, new industries of the highest importance have been established, and older industries have been revolutionised; and at the conclusion of this chapter we may appropriately devote a little space to the discussion of some of the more important cases in which catalysis has found an application in industrial chemistry. In succeeding chapters other applications of catalysis will be met with.

Manufacture of Sulphuric Acid.

Sulphuric acid, or oil of vitriol, the discovery of which dates from the fifteenth century, is one of the most important substances in our modern civilisation. Not only is it used in the older process of manufacture of soda and of hydrochloric acid, but also in the production of nitric acid and of explosives, in the manufacture of dyes, fertilisers, glucose, and alum, and in most chemical and metallurgical industries. Owing to the great development last century of the soap and cotton industries, with their great demand for soda and bleaching powder, England became the chief producer of sulphuric acid, and supplied most of the world with this indispensable chemical. But this has now been changed. Owing to the march of science and the development of chemical industries in other countries, the position has completely altered, and Great Britain now ranks only third in the list of producers of sulphuric acid, the total annual consumption of which throughout the world amounts to about 5,000,000 tons.

The reaction on which the production of sulphuric acid

depends is the oxidation of the gas sulphur dioxide to form the compound sulphur trioxide, which combines readily with water to give the compound known as sulphuric acid. The difficulty is, however, met with that combination between sulphur dioxide and oxygen does not take place appreciably at the ordinary temperature; and when one seeks to hasten on the combination by raising the temperature, another difficulty is encountered. As the temperature is raised the rate at which the sulphur dioxide and the oxygen combine certainly increases, as we have already learned to be universally the case, but as the temperature rises the *extent* to which combination takes place becomes less and less, by reason of the fact that at high temperatures the sulphur trioxide decomposes again into sulphur dioxide and oxygen. The result, therefore, is that at a temperature at which the combination of sulphur dioxide and oxygen would take place sufficiently rapidly, the amount of sulphur trioxide formed is too small to allow of the process being commercially successful. We now know, however, the direction in which to look for a way out of the difficulty. We must find a catalyst which will so accelerate the rate of oxidation of the sulphur dioxide that the process may be carried out with sufficient rapidity at a temperature so low that the decomposition of the sulphur trioxide is negligible. Such a catalyst was found at an early date in the oxides of nitrogen, and since the year 1746 the manufacture of sulphuric acid has been carried on in this country by a process depending on the use of these oxides. This method of manufacturing sulphuric acid consists, essentially, in passing sulphur dioxide, obtained by burning sulphur, or by heating iron

pyrites (sulphide of iron) or the spent oxide of iron from gas-works, etc., together with air, oxides of nitrogen, and steam, into a series of large leaden chambers. Here the sulphur dioxide combines with the oxygen of the air under the catalytic influence of the oxides of nitrogen, and the sulphur trioxide formed combines with the steam to form sulphuric acid. The acid produced in this "leaden chamber process," as it is called, is a rather impure aqueous solution of sulphuric acid (known as brown oil of vitriol), and must be subjected to processes of purification and concentration before the pure acid is obtained.

At the beginning of the present century, however, a revolution began to take place in the process of manufacture. This was due mainly to the successful development of the process of manufacture of synthetic indigo, which necessitated the use of the very powerful reagent obtained by the addition of sulphur trioxide to pure sulphuric acid, and known as fuming sulphuric acid.

It had been observed as far back as the year 1831 by a vinegar manufacturer of Bristol, Peregrine Phillips by name, that the oxidation of sulphur dioxide by oxygen is greatly accelerated by the presence of platinum, just as we have seen that this metal also accelerates the combination of hydrogen and oxygen; and this observation gave rise to many hopes of an improved method of manufacturing sulphuric acid. Even in 1835 a well-known French chemist, Clement-Desormes, gave expression to the conviction that in ten years at most it would be possible to manufacture sulphuric acid directly from its constituents, without the use of leaden chambers and nitric acid. But the unwisdom of prophecy is proverbial,

and the period of ten years lengthened out to one of nearly seventy, before the ability and persistence of the technical chemists in one of Germany's greatest chemical works succeeded in developing the discovery of Peregrine Phillips into a successful industrial process.

When the attempt was made to utilise the "contact process," as it is called, for the commercial production of sulphuric acid, a difficulty was met with which delayed success and threatened complete failure. The production of sulphur trioxide which at first took place with great readiness soon began to diminish, and after some time ceased altogether. The platinum lost its catalytic activity. On investigation, this loss of activity was found to be due to a "poisoning" of the platinum—a phenomenon to which we have already referred—and the substance which was found to be chiefly responsible for this was arsenic. This arsenic was derived from a small amount of impurity contained in the iron pyrites, a naturally occurring sulphide of iron used as the source of the sulphur dioxide, and it was only after much labour that a means was found of ridding the gas of all traces of this poison. When this had been done, the contact process could be carried out with success.

For the production of sulphuric acid by the contact process, the enormous leaden chambers, with a capacity sometimes of 150,000 cubic feet, are replaced by comparatively small, cylindrical vessels containing a number of tubes filled with platinised asbestos[1]; that is, asbestos on which finely divided platinum has been deposited. Through these tubes, which are maintained at the proper

[1] Oxide of iron can also be used as a catalyst.

temperature by the heat given out in the reaction, the mixture of sulphur dioxide and oxygen (or air) is passed. The oxidation of the sulphur dioxide takes place rapidly and practically completely, and the sulphur trioxide issues from the apparatus as a white mist, which is then passed into a solution of sulphuric acid containing about 98 per cent. of acid. In this way a pure sulphuric acid, as well also as the powerful fuming sulphuric acid to which we have referred, can readily be obtained.

Whether the contact process will eventually succeed in entirely superseding the older leaden-chamber process, it is impossible to say; for, under the stimulus of competition, improvements have been effected in the latter process which will in any case retard, if they do not altogether prevent, its complete disappearance.

Hardening of Fats.

Another industry of recent but rapidly increasing growth, which depends on the application of catalysis, is that of the conversion of liquid oils into solid fats; a process generally, if erroneously, referred to as the hardening of fats.

It has already been pointed out (p. 33), that the animal and vegetable fats and oils are, essentially, compounds of glycerine with acids, such as palmitic, stearic, and oleic acids. The glycerine compounds of the saturated palmitic and stearic acids (p. 33), are solid, and constitute the main portion of the hard fat, beef suet. The glycerine compound of the unsaturated oleic acid is, however, a liquid, and is

the chief constituent of olive oil; and the other natural animal and vegetable oils are also mainly compounds of glycerine with unsaturated acids. For these different fats and oils there are, at the present day, two main uses; namely, as foodstuffs, to supply the body with the necessary amounts of carbonaceous matter, and for the purpose of making soap. So far as foodstuffs are concerned, butter, or the fat of milk, constitutes a large part of the fatty material consumed. Owing, however, to the increase of population and to the rising price of butter, the problem of obtaining some substitute for this very important article of food became of increasing importance. The solution of the problem we owe to French ingenuity, and the industrial production of butter substitutes, *e.g.* margarine, which dates from 1870, has now attained to very great dimensions. Beef-fat or hog's lard, after being melted and clarified, is separated from the oil which it contains, and mixed in churning machines with various vegetable oils, such as cotton-seed oil, soya-bean oil, cocoa-nut oil, palm-kernel oil, and also with milk, and in this way a material is obtained which can be used as an efficient substitute for butter. But since these butter substitutes are derived mainly from animal fats, the supply of solid fats necessary for the manufacture of soap has been seriously diminished; and it became, therefore, a matter of great importance to discover a method by means of which liquid oils could be converted into solid fats. Theoretically, the process is a simple one. Oleic acid, for example, differs from stearic acid only in the fact that it contains less hydrogen. It is what we have called an unsaturated compound, and if we add the proper amount of hydrogen to the oleic acid, we

shall convert it into the solid stearic acid; or, on the other hand, if we add the hydrogen to the liquid glycerine oleate, we shall convert it into the solid fat glycerine stearate; and similarly with the other unsaturated compounds present in other oils. Although it was not difficult to carry out such a conversion in the laboratory, no commercially successful process was discovered until it was found that finely divided nickel acts as an efficient catalyst. In the presence of this metal, the liquid oils, olive oil, linseed oil, fish oil, etc., combine readily with gaseous hydrogen and become converted into solid fats suitable for use in the manufacture of soap.

Not only does the introduction of this process offer to the soap boiler a fresh source of the material which he requires, but it also permits of the profitable employment of substances for which formerly comparatively little use could be found. Thus, for example, whale oil, which on account of its unprepossessing taste and smell found formerly but little application, is now converted in large amount, by the above process, into a solid, odourless material suitable for the making of soap.

This recent discovery of chemical science, which is chiefly worked in England by the firm of Messrs. Crosfield and Son, promises to be one of far-reaching importance. Not only does it secure a fresh source of raw material for the manufacture of an article of such importance in our modern civilisation as is soap, and thereby prevent a rapid rise in the cost of its production, but by stimulating the cultivation of oil-producing plants, it will exercise a profound influence on the economic development of those

countries which are suitable for such cultivation. Of the importance in the service of man of this modern industrial process, founded as so many industrial processes are on investigations of apparently purely scientific interest, it is impossible to form an estimate.

CHAPTER VII

FIXATION OF ATMOSPHERIC NITROGEN

OF all the chemical elements of which our text-books describe the properties, none, perhaps, was, until a few years ago, so uninteresting as nitrogen. From the time of its discovery by the botanist Rutherford in 1772, down almost to the present day, scarcely a property or character of a positive nature was ascribed to the element. Its properties were negative properties, and were described in negative terms. Useless when alone, it stubbornly resisted almost all attempts to make it associate with its fellow-elements; and it played, at best, the *rôle*—again negative in character—of acting as a drag on the too vigorous activity of the atmospheric oxygen.

That an important part in the economy of nature had, nevertheless, been assigned to this element, was abundantly clear from the fact that it is an essential constituent of the most important animal and vegetable materials, a constituent without which life itself is impossible. With few exceptions, however, plants are unable to absorb and utilise elementary nitrogen, which exists abundantly in the air; and they must therefore be supplied with combined nitrogen in such forms as they can assimilate. Animals are equally incapable of assimilating elementary

nitrogen, and are dependent on plant food for their supply of nitrogen compounds.

Owing to the apparent impossibility of coaxing the enormous store of elementary nitrogen contained in the air into suitable combination with other elements, mankind contented itself, resignedly if not complacently, with the natural sources of supply of useful nitrogen compounds; and this position was all the easier to adopt as the natural supply was sufficient for the needs of the day. In 1898, however, Sir William Crookes, as President of the British Association, delivered the solemn warning that the years of plenty were quickly passing. The supply of wheat, the staple foodstuff of Western peoples, from all the land available for cultivation, would soon be insufficient to provide for the needs of the growing population unless the yield of the soil could be greatly increased by intensive cultivation, which in its turn would, in a few years, exhaust all the known sources of combined nitrogen. Famine, therefore, stared them in the face, and there would be no Egypt from whose granaries supplies could be obtained.

It is unnecessary to discuss whether the warning given by Sir William Crookes was too alarmist or not; there was undoubtedly need for the warning to be given. If the produce of the wheat-bearing lands was to keep pace with the increase in the population, more intensive cultivation must be resorted to, and ever-increasing quantities of nitrogen compounds must therefore be applied to the soil. But the world's demands for compounds of nitrogen were rapidly increasing, not only for purposes of agriculture, but in other directions also. For the manufacture of

dynamite, gun-cotton, and other explosives, as well as for the production of dyes, the demand for nitric acid goes on increasing; for the manufacture of sodium carbonate or soda there is an ever-growing demand for ammonia; and so it is also with regard to the cyanides, used in connection with the extraction of gold from its ores, and the plating of metals.

But while the demand for nitrogen compounds was increasing rapidly, the sources of supply showed no such elasticity. The main sources of supply were the following:—

(1) Matter of vegetable origin: Vegetable refuse, nitrogen compounds in the humus of the soil, etc.

(2) Matter of animal origin: Animal manures, fish meal, guano, coprolites, etc.

(3) Ammonium compounds from coal, lignite, peat, silt.

(4) Mineral deposits: Saltpetre (from the Indian nitre plantations), Chile saltpetre.

(5) Combined nitrogen in rocks.

(6) Absorption of free nitrogen by nodules on the roots of leguminous plants, through the agency of bacteria.

Of the above sources of supply it may be said that the waste animal and vegetable materials, although of great local importance, do very little to relieve the general situation; the supply of fish meal is strictly limited, and the guano deposits are nearing the point of exhaustion.

Of very considerable importance is the supply of ammonium compounds from coal, peat, etc. The following table gives the total amount of ammonium sulphate obtained annually from the distillation of coal:—

WORLD'S PRODUCTION OF AMMONIUM SULPHATE.

	Tons.
1902	543,000
1908	852,000
1909	978,000
1910	1,111,800
1911	1,181,000

The maximum amount obtainable if all the coal mined were distilled or coked would be 11,800,000 tons.

In coal, therefore, we have a very valuable source of supply of combined nitrogen, a fact which adds weight to the arguments put forward on the ground of economy in a previous chapter, in favour of the preliminary carbonisation or coking of coal, with recovery of the ammonia as by-product. But, on the other hand, it must be remembered that the coal supply itself is not inexhaustible, and the recovery of ammonia from coal, therefore, while it might postpone could not avert the danger of which Sir William Crookes gave warning.

On the other hand, there are two very valuable sources of ammonia which have not yet been exploited as they might be. When peat is carbonised, the nitrogen present can be recovered to a large extent as ammonia, and in view of the enormous peat moors which exist in the world (in Russia there are no fewer than 95,000,000 acres, and in Finland, 18,500,000 acres), the reserve stock of nitrogen is very great. It seems certain, therefore, that the process of carbonisation of peat, with production of a power gas and recovery of the nitrogen present, as ammonia, might be developed in many regions as it has already been developed in some, into a profitable industry. All attempts made in this direction should certainly be welcomed and encouraged.

Another important source of ammonia is the blast furnace. At the present time, over 12,000 tons of ammonium sulphate are obtained from blast furnaces in Great Britain alone; and it seems that this amount might be largely increased.

But by far the most important natural source of combined nitrogen at the present time is found in the deposits of sodium nitrate or Chile saltpetre, which occur in the rainless districts of South America. These deposits have not only been the main source of supply of the nitrogen compounds used in agriculture, but they have also furnished practically the whole of the material used for the manufacture of nitric acid and of potassium nitrate. As a consequence, the demands made on these deposits have gone on increasing, as is evident from the following table:—

EXPORT OF CHILE SALTPETRE.

	Tons.
1830	1000
1850	25,000
1890	1,000,000
1900	1,454,000
1902	1,379,000
1904	1,497,000
1906	1,732,000
1908	2,052,000
1910	2,324,000
1911	2,449,000

The value of the annual production now amounts to over £24,000,000.

But the nitrate beds although enormous are not inexhaustible, and whether the time of exhaustion lies distant fifty years, as some have estimated, or a hundred and fifty years, it is obvious that the situation in 1898 was one which might well cause grave concern. Sir William

Crookes, therefore, was surely only doing his duty in calling the attention of his countrymen and of the world to the inevitable disaster which threatened unless some fresh means were found of obtaining combined nitrogen. As the discovery of any considerable new supplies of naturally occurring nitrogen compounds was scarcely to be relied on, there was an imperative demand laid on chemists to discover some means of forcing the inexhaustible store of elementary nitrogen into such a state of combination that its assimilation by plants is rendered possible. As Sir William Crookes said: "The fixation of atmospheric nitrogen is one of the greatest discoveries awaiting the ingenuity of chemists." And the ingenuity of chemists, assisted by the engineers, has proved itself equal to the task. During the past eight or nine years not one but several methods have been discovered by means of which the atmospheric nitrogen can, on a large scale and in a commercially successful manner, be forced into useful combination with other elements. Indeed, so far as nitrogenous fertilisers are concerned, the prospect of a wheat famine has now been removed to an indefinitely remote future.

1. *Direct Combination of Nitrogen and Oxygen.*

Since the atmosphere consists essentially of a mixture of nitrogen and oxygen, it is obviously most natural that attempts should be made to bring about the combination of these two gases. That this combination does actually occur under suitable conditions, was shown as long ago as 1784 by Cavendish and by Priestley. Cavendish, for example, had shown that when electric sparks are passed

through air, oxides of nitrogen are formed; and by absorbing these oxides in water or in alkalies, nitric acid or nitrates could be obtained. The possibility of obtaining nitric acid from the air was therefore proved, and the difficulty which faced the chemist and engineer was that of applying the scientific fact and of developing it into a commercially successful process. Into the history of the attempts to overcome this difficulty, it is not possible to enter here, and I must restrict myself to a very brief description of the processes which are in successful operation at the present day.

Before we enter on a discussion of these processes, however, a few words are necessary on the theory of the chemical reactions involved, on the recognition of which the success of the processes depends.

In the first place one must note an important respect in which the combustion of nitrogen, or the combination of nitrogen with oxygen, differs from the combustion, say, of hydrogen. When hydrogen burns, a large amount of heat is given out, and consequently, when a mixture of hydrogen and oxygen is ignited at any point, the temperature of the surrounding gas is raised to the ignition point and the flame spreads throughout the whole mixture. But in the case of nitrogen and oxygen, combination takes place with *absorption* of heat—the reaction is an endothermic one—and heat must therefore be continually added to the mixture in order to allow the process of combustion or combination to proceed. Indeed, if it were not so, a flash of lightning would set the whole atmosphere ablaze, and "deluge the world in a sea of nitric and nitrous acids."

Further, the reaction between nitrogen and oxygen whereby the compound nitric oxide is formed, is a reversible reaction (p. 92), represented by the expression—

$$N + O \rightleftarrows NO$$

and at a given temperature, therefore, only a certain proportion of the gases combines. But it is a general rule that in such a case, the reaction which takes place with absorption of heat is favoured by raising the temperature; and it is therefore to be expected that as the temperature is raised, the proportion of nitric oxide produced will become greater and greater. This prediction from theory was confirmed by experiment, as the following numbers show :—

Temperature.	Volumes of nitric oxide in 100 volumes of gas.
2800° F.	0·37
2919° F.	0·42
3200° F.	0·64
4185° F.	2·05
4356° F.	2·23
5301° F.	5

It is clear, therefore, that in order to obtain as large a proportion of nitric oxide as possible, it is necessary to conduct the reaction at as high a temperature as possible. And this carries with it another advantage, for the higher the temperature, the more rapidly does the combination of oxygen and nitrogen occur; the sooner, therefore, is the equilibrium concentration of nitric oxide reached. This is seen from the following figures :—

Temperature.	Time required for the production of equilibrium.
1832° F.	82 days
2732° F.	1·25 ,,
3812° F.	5 seconds
4532° F.	0·01 second

But there is one important point to bear in mind. Since the reaction is a reversible one, decomposition of the nitric oxide will take place as the temperature is lowered; and just as high temperature increases the velocity of combination, so also it will increase the velocity of decomposition. It is, therefore, of the greatest importance that the mixture of gases, after equilibrium has been established at a high temperature, shall be cooled down as rapidly as possible to a temperature at which the velocity of decomposition is comparatively slow, to a temperature, say, of about 2000° F.

Let us now see how these different requirements which theory and laboratory experiments show to be necessary, are realised in industrial practice.

The first successfully to solve the problem of the combination of nitrogen and oxygen on a commercial scale, were two Norwegians, Birkeland and Eyde. For the production of the high temperature required, they made use of the electric arc, the only means whereby a temperature of from 5000° to 6000° F. can be satisfactorily and economically obtained; and the arc, produced by an alternating current, was caused to expand out into a circular sheet of flame by the action of a powerful electromagnet. The arc, expanded in this way into a sheet of flame about two yards in diameter, is formed in a furnace of circular shape, a section through which is shown in Fig. 9. The flame chamber is of fire-brick, pierced by channels through which air can be fed into the flame, and the fire-clay is cased in iron. From the flame-chamber, the temperature of which may rise from 5000° to 6000° F., the hot gases are led away through channels in the

periphery of the furnace, and are cooled rapidly to a temperature of about 1800° to 1900° F., the heat which is given up by the gases being used in boilers for the production of steam. When sufficiently cooled, the gases

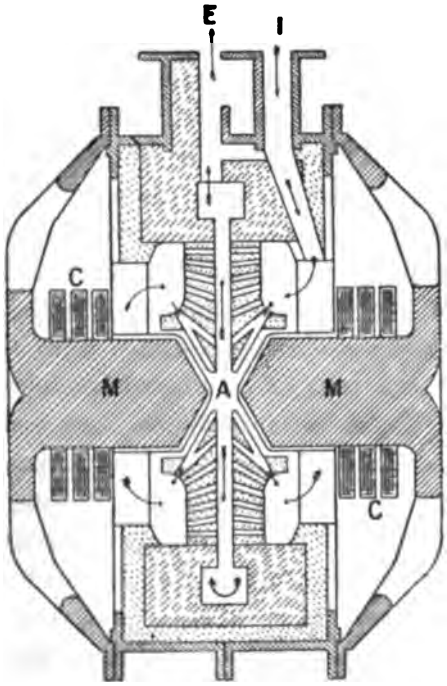


FIG. 9.—BIRKELAND AND EYDE FURNACE.

Air, entering at I, passes as shown by the arrows to the centre of the furnace in which the electric arc, formed at A, is spread out into a disc of flame by means of the electro-magnet M M. The gas then passes out at E. C C are the coils of wire through which the electric current passes in order to actuate the electro-magnet.

are passed into chambers lined with acid-proof stone, where time is given to the nitric oxide to combine with the free oxygen present in the mixture of gases and so to form a higher oxide called nitrogen peroxide, NO_2.

From the oxidation chambers, the gases pass on through a series of absorption towers, the first of which contains broken quartz over which a fine stream of water is allowed to trickle. The greater portion of the nitrogen peroxide is absorbed by the water and gives rise to nitric acid. For the purpose of removing the last traces of the oxides of nitrogen, the gases are caused to pass through a second series of absorption towers, down which trickles a solution of sodium hydroxide (caustic soda), and in these towers sodium nitrite is produced. The nitric acid obtained from the first series of towers is neutralised by means of limestone (carbonate of lime), and the solution of nitrate of lime (calcium nitrate) is concentrated by evaporation under reduced pressure. When sufficiently concentrated, it is pumped on to cold revolving cylinders on which the liquid rapidly solidifies, and from which it can then be scraped off in flakes. This nitrate of lime is known as Norwegian saltpetre, or air saltpetre, and it can be used directly, like Chile saltpetre, as a fertiliser. A certain amount of the nitric acid is also used for making nitrate of ammonia (ammonium nitrate), the richest of all nitrogen fertilisers. For this purpose the ammonia, in solution, is imported from England, converted into ammonium nitrate by the addition of nitric acid, and exported again in this form to England.

The sodium nitrite obtained from the second series of absorption towers is used in large quantities, more especially in Germany, in the manufacture of dyes.

Besides the one invented by Birkeland and Eyde, other types of furnace have also been introduced, such as the Schönherr furnace in which a long cylindrical flame

is produced in a tubular furnace, and the Pauling furnace, in which a flame of burning gas is obtained by blowing a stream of air through an electric arc formed between ⅄⅄-shaped terminals.

The production of nitric acid and nitrates by the direct combination of atmospheric nitrogen and oxygen, is carried out mainly, though not entirely, at Notodden and other parts of the Telemark district in Southern Norway, where an abundant and very cheap water-power is available. At Notodden there are two power stations capable of supplying 60,000 h.p., but at Vemork, near the Rjukan waterfall, some distance away, two other power-stations, capable of supplying 250,000 h.p., have recently been constructed. To ensure a constant water supply for these two power-stations, a dam was constructed a short distance below Lake Mös, whereby a reservoir was created with a storage capacity of about 190 thousand million gallons, an amount nearly equal to that retained by the great barrage at Assouan.

With the advantages which Southern Norway possesses, it is possible to produce synthetic nitrates at a cost considerably lower than that of Chile saltpetre. At present the annual output is about 160,000 tons; a large amount, certainly, although only a small proportion of the world's annual consumption.

2. *Fixation of Nitrogen by means of Carbides.*

The process of direct combination of nitrogen and oxygen demands for its success a very cheap electric power, and it can therefore be carried out only at a few

places where an abundant water-power can be made available at a low cost. But other processes for the fixation of atmospheric nitrogen have been discovered since the beginning of the present century in which the cost of electricity is not such an important factor, and which can therefore be carried out with commercial success even when the electrical power is somewhat expensive.

In one of these processes, the starting-point is the compound calcium carbide which, as we have seen, is now manufactured in large quantities for the production of acetylene. When nitrogen is passed over this carbide, suitably heated in retorts, a reaction takes place with formation of a compound known as calcium cyanamide, and the production at the same time of a quantity of carbon. The dark grey coloured mixture which is thus obtained, and which contains about 60 per cent. of calcium cyanamide, is put on the market under the name of *nitrolim*, or *lime nitrogen*, as it is called in America.

For this compound, calcium cyanamide, quite a number of uses have been developed, but the most important is that as a source of nitrogen in agriculture. When properly applied to the soil, calcium cyanamide has been found to have a fertilising value for cereals nearly equal to that of ammonium salts. But the physical qualities of the commercial nitrolim, its dustiness and dirtiness, were prejudicial to its use, and although the former defect has been largely removed, much of the cyanamide is used, not directly as a fertiliser but for conversion into ammonium salts, ammonia being readily obtained by passing superheated steam over the cyanamide.

In the previous chapter I endeavoured to emphasise how man had learnt to avail himself of the catalytic activity of certain substances and to make them work for him at no expense, and here, in connection with the economic utilisation of Nature's boundless stores of nitrogen, catalysts have again been made to play an important part.

Just as we have seen (p. 97) that hydrogen burns to water with great vigour, even at the ordinary temperature, in the presence of platinum, so also it was found that when a mixture of ammonia and air (or oxygen) is passed over platinum, the ammonia burns and forms nitric acid. By a proper regulation of the process, it is possible to effect the combustion of only half of the ammonia, the other half then combining with the nitric acid produced to form nitrate of ammonia. It is in this direction that the manufacturers of cyanamide are apparently now turning their attention.

It is perhaps worth while to emphasise here the importance of this application of catalysis. Not only can it be used as a convenient method of obtaining the valuable fertiliser nitrate of ammonia, but it can be used also for the purpose of obtaining nitric acid. For the most part this acid, the indispensable necessity of which in the manufacture of explosives has already been pointed out, is prepared from Chile saltpetre, and it is therefore clear that a country whose supplies of this salt might be cut off, would, in time of war, be rendered powerless. It was, indeed, under the stimulus of the apprehension that such might be the fate of his country, that the German chemist, Professor Ostwald, addressed himself to the

successful development of the process of burning ammonia to nitric acid, to which we have just referred. The necessary ammonia can be obtained by the distillation of coal, by the decomposition of calcium cyanamide, and also, as we shall see, by the direct combination of nitrogen and hydrogen. This synthesis of ammonia, indeed, is perhaps the most valuable method of utilising the atmospheric nitrogen, and to its consideration we must now turn our attention.

3. *Synthetic Production of Ammonia.*

However important the processes to which we have referred may be, and however great the contribution which they have made towards a solution of the "nitrogen problem," they could scarcely, on account of their greater or less dependence on cheap electric power, furnish a complete solution of the problem. Something more was needed, and the announcement some years ago that the direct combination of nitrogen and hydrogen to form ammonia had been developed into a commercially successful process, was recognised as of the highest significance and importance.

The problem of successfully bringing about the direct combination of nitrogen and hydrogen is one which has taxed the ingenuity of chemists for many years. Inert as the two gases are towards each other at the ordinary temperature, it was well known that by the passage of electric sparks through a mixture of the two gases, ammonia was produced, but only in very minute amount. It was, moreover, also known that when electric sparks

are passed through gaseous ammonia, decomposition, almost but not quite complete, into nitrogen and hydrogen takes place. In other words, it was known that the reaction between nitrogen and hydrogen is a reversible one, and leads therefore to a state of equilibrium; but the concentration of ammonia present was exceedingly small and all attempts to obtain an appreciable amount of the compound by direct combination of nitrogen and hydrogen ended in failure. But new weapons were being forged, the weapons of chemical dynamics, and with these the problem was again attacked, and only within the past few years, as the result of ably-directed and painstaking endeavour, the problem has been solved.

Experiment has shown that when nitrogen and hydrogen combine, the volume of the ammonia produced is less than that of the mixed hydrogen and nitrogen; and therefore, according to the laws of chemical dynamics, the relative amount of ammonia produced will be increased by bringing the gases together under a high pressure. Moreover, contrary to what was found to be the case in the combination of nitrogen and oxygen (p. 118), combination of nitrogen and hydrogen takes place with *evolution* of heat; and therefore (p. 93, footnote), the formation of ammonia will be favoured by keeping the temperature *low*. The following table will show how the predictions of theory were borne out by experiment:—

Temperature.	Percentage amount of ammonia in the equilibrium mixture when the pressure was	
	1 atmosphere	100 atmospheres
1472° F.	0·011	1·1
1292° F.	0·021	2·1
1112° F.	0·048	4·5
932° F.	0·13	10·8

In order, therefore, to attain success in the industrial synthesis of ammonia from its elements, the rule must be borne in mind: Maintain the gases under as high a pressure and at as low a temperature as possible.

But here again we meet with that factor which so sharply distinguishes success in the scientific laboratory from success in the factory, the factor of time. At about 900°, it is true, quite an appreciable amount of ammonia is formed by the direct combination of hydrogen and nitrogen, but the *rate* at which this amount is produced is so slow that the process would be industrially useless. Again, therefore, the first immediate requirement is the discovery of a suitable catalyst, and such a catalyst was found in osmium, in uranium, in iron, and in certain other substances, some of which previous investigators had also employed, but without achieving success. And here again, as in other cases to which reference has been made, failure was due to a non-recognition of the fact that catalysts can be "poisoned." Through the presence of minute traces of different impurities in the nitrogen or hydrogen, the efficiency of the catalyst can be destroyed, and it was only by laborious and careful investigation of the behaviour of different catalysts and of the behaviour of other substances towards these catalysts, that success was made possible. Nor indeed were the engineering difficulties much less than the chemical, but they have been overcome, and the synthetic production of ammonia has now been added to the industries of the world.

In the manufacturing process, a mixture of nitrogen, and hydrogen, under a pressure of 150–200 atmospheres, is circulated, by means of a pump, over the catalyst contained

in a tube heated electrically to a temperature of about 930° F. After passing over the catalyst, the gases, which now contain a certain proportion of ammonia, are passed through a tube immersed in a freezing mixture, so as to liquefy the ammonia, while the unchanged nitrogen and hydrogen are made to circulate again over the catalyst.

The importance of this synthetic process for preparing ammonia lies in the fact that its success is not dependent on a cheap supply of electrical power, and that it can therefore be carried out in countries which are unfavourably situated for the production of the electricity required in the previous methods of "fixing" the atmospheric nitrogen. By this process one is enabled not only to produce the nitrogenous fertiliser, sulphate of ammonia, which is so valuable in agriculture, but, by the catalytic oxidation of the ammonia, one can obtain nitric acid, and the nitrates, which are so essential for the manufacture of explosives. From the last mentioned compounds, also, is prepared the nitrite of soda, of which enormous quantities are consumed in the manufacture of dyes.

4. *Combination of Nitrogen with Metals.*

But there is one other process for the fixation of atmospheric nitrogen which promises to have much success, especially in France, where the process is already being worked, and in the other countries where the necessary ores of aluminium exist. According to what is known as the Serpek process, nitrogen is passed over a heated mixture of bauxite (naturally occurring aluminium oxide), and coal. Combination takes place between the nitrogen

and the aluminium with formation of a compound known as aluminium nitride, and when this is boiled with water, almost the whole of the nitrogen present is liberated as ammonia, while the aluminium is obtained in the form of pure oxide, suitable for use in the production of the metal. Although by this process sulphate of ammonia can be produced at a low cost, the successful development of the process is intimately bound up with the demand for pure oxide of aluminium; and this, in turn, depends on the demand for the metal.

From what has now been said, it may be agreed that the outlook with regard to the supply of nitrogen compounds for agricultural and industrial operations is full of hope; and although the atmospheric nitrogen has, as yet, only been made to satisfy a small part of the world's demands, no difficulties stand in the way of a greatly increased supply by one or all of the processes which I have attempted to describe. And chemists surely may justifiably feel some pride and satisfaction, and may even reasonably look for some sign of appreciation on the part of their fellow men, in the fact that in the solution of the great problem of the fixation of atmospheric nitrogen, their ingenuity has not altogether been found wanting. To make two ears of corn to grow where only one grew before, is an achievement which should surely win for science some larger measure of popular recognition and esteem.

But when we contemplate the position which our own country occupies in this matter, we must confess to a feeling of great disappointment. Norway, Germany, Austria, Italy, France, the United States, Canada, India,

Japan, in fact, practically every civilised country but our own, is actively engaged in developing the nitrogen industries. It is true that we produce a considerable quantity of ammonia in our gas-works, and other works, and we are also, on a very small scale, producing ammonia from peat. But we are thereby merely using up resources which cannot be replaced, and we are doing nothing to create further supplies of the vitally necessary compounds of nitrogen. We export our coal to Odda and buy it back again, at an enhanced price, as calcium cyanamide; we export our ammonia to Notodden, and buy it back as ammonium nitrate. It is often stated that we are at a disadvantage in this country in not having at our disposal the cheap water-power which is available in some other countries at least. But it has also been pointed out by competent authorities that electrical power could be developed in this country at a price which would allow of the successful working more especially of the cyanamide process. Moreover, we must bear in mind that the synthetic production of ammonia which has only within the past few years been developed in Germany, is not dependent on specially cheap power at all. Surely the time is more than come for some effort to be made to produce within our own borders those substances which are of such vital importance in the life of our people.

Even the simplest process of chemical manufacture involves, as a rule, the working together of several processes, each of which forms a detail in the complete series of operations; and the success of the process as a whole depends on the efficiency with which the preliminary

and detail processes can be carried out. Thus, in the nitrogen industries, for example, it is essential for success that a cheap source of pure nitrogen and also, in the case of the synthetic production of ammonia, a cheap source of hydrogen should be available.

For the purpose of obtaining nitrogen the method which is most frequently employed on the manufacturing scale is the distillation of liquid air. Liquid air, of course, consists of a mixture of liquid nitrogen and liquid oxygen, which boil at $-319°$ and $-296{\cdot}5°$ F. respectively. Just as we saw that the different hydrocarbons in crude petroleum can be separated by fractional distillation, so also in the case of liquid air, we can separate the nitrogen from the oxygen. As the nitrogen has the lower boiling-point, it distils off first, and by suitable arrangements can be obtained free from oxygen.

The production of liquid air is now a very simple matter, and has already developed into an industry of very considerable proportions. At Niagara Falls, for example, two million cubic feet of nitrogen are prepared from the air daily, by the distillation of liquid air; and the scale on which the liquefaction of air is carried out may be gathered from the fact that this liquid is thrown to waste at the rate of thirty gallons an hour, merely to keep the apparatus flushed out and in good order. The principle on which the process of liquefaction depends is that when highly compressed air is allowed to expand rapidly its temperature falls; and the amount by which the temperature is lowered on expansion is all the greater the lower the temperature of the compressed gas previous to the expansion.

The industrial application of this principle is due mainly to a German and an English engineer, Linde and Hampson, and their method will be understood from Fig. 10. Air under a pressure of about 150 atmospheres, and free from moisture and carbon dioxide, enters the apparatus at A, and passes, as shown by the arrows, to the central tube, where it sub-divides into a series of three or four tubes, B, of thin copper wound spirally round the central rod D. At the lower end, these tubes pass together into a valve C, at which the compressed air rapidly expands. A lowering of temperature is thereby produced. The cool air now passes upwards over

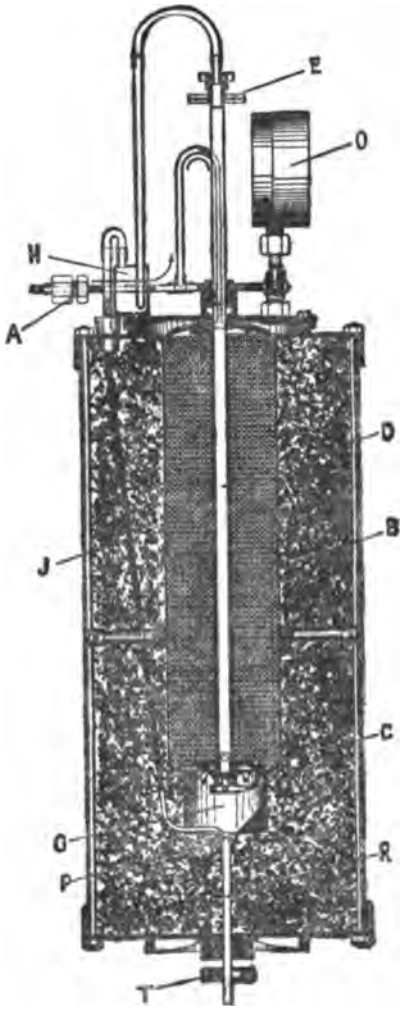


FIG. 10.—HAMPSON APPARATUS FOR LIQUEFYING AIR.

A, tube by which air enters; B, section through spirals of copper tubing; C, expansion valve; D, central spindle; E, wheel for opening and closing expansion valve; G, tank in which liquid air collects; H, gauge to indicate amount of liquid air in G; J, tube connecting tank with gauge; O, pressure gauge to indicate pressure at which the air enters the apparatus; P, valve closing tube R, through which the liquid air is withdrawn; T, wheel for opening the valve P.

the layers of copper tubing, and so cools down the compressed air which is passing through these towards the expansion valve. In this way the air expanding at the valve gets progressively colder and colder, until at last a point is reached when the lowering of temperature on expansion is so great that the air liquefies. It collects in the tank E, from which it can be drawn off from time to time through the tube R.

This apparatus can also be made use of for the cheap production of hydrogen on a commercial scale, use being made of water gas (a mixture of carbon monoxide and hydrogen), as the source of the hydrogen. By liquefying this mixture of gases in the Linde apparatus, a practically complete separation of the two gases can be effected by distillation, as in the case of nitrogen and oxygen, and the last traces of carbon monoxide can be readily removed by suitable chemical absorbents.

A large amount of hydrogen is also prepared by passing a current of electricity through a solution of caustic potash or of potassium carbonate. In this process oxygen is also produced, and the process can be economically carried out at places where there is a demand for the two gases.

The ease with which liquid air can now be produced is not only of great industrial importance, but is also of much value in the furtherance of scientific knowledge. By means of liquid air, one is enabled to extend the scope of scientific investigation to temperatures which otherwise would be inaccessible; and the increase of knowledge which has accrued therefrom is of the highest scientific interest and practical value. The utilisation of this new

aid to scientific research was greatly facilitated by the introduction of the well-known Dewar "vacuum vessels." These "vacuum vessels," which are now so familiar under the name of "thermos" flasks, consist of double-walled glass vessels (Fig. 11), the air being removed as completely as possible from the space between the two walls. The "vacuum" by which the vessel containing the liquid air is thus surrounded, acts as a very efficient heat insulator, so that although the liquid air is several hundred degrees colder than the surrounding atmosphere, the heat from the latter is conducted only very slowly to the liquid air, which may thus be preserved for hours without any considerable loss.

FIG. 11.—DEWAR VACUUM VESSEL.

CHAPTER VIII

GLASS, SODA, SOAP

IN the previous chapter we discussed one of the youngest of the chemical industries, an industry which has been developed at the call of necessity to contribute to the well-being of man and the advance of civilisation. In the present chapter we shall turn our attention, in the first place, to one of the oldest industries, which by reason of the unique and valuable properties of the product, is still one of the foremost industries of civilised countries, the industry of glass making.

Many, doubtless, are familiar with the legend reported by the Roman writer Pliny in the first century of our era, which ascribed the discovery of glass to a party of Phœnician sailors who were forced by stress of weather to land on the sandy shore under Mount Carmel. Here, standing their cooking-pots on lumps of soda, with which their ship was laden, they observed the soda and the sand to fuse together under the heat of the fire, and so to form a glass. But we can be sure that it was not thus that glass was discovered, and although the Phœnician towns of Tyre and Sidon were, at an early period, almost as celebrated for their glass as for the famous purple dye which coloured the robes of kings, it is to Egypt

that we must look for the first knowledge of glass or glass-like material; to that country which, as Herodotus wrote, "contains more wonders than any other land, and is pre-eminent above all countries of the world for works which almost baffle description." The representation of the art of glass-blowing on the walls of the tomb of Tih (about 3800 B.C.), with which every visitor to Egypt is familiar, and the discovery of glass beads and ornaments among the ruins of the ancient city of Memphis, bear testimony to a knowledge of this material at a very early period in Egyptian civilisation. What mankind owes to the first discoverer of the process of making glass, it is scarcely possible to describe. That first artificer in glass, as Dr. Johnson wrote, "was facilitating and prolonging the enjoyment of light, enlarging the avenues of science, and conferring the highest and most lasting pleasures; he was enabling the student to contemplate nature and the beauty to behold herself." And in recent years glass has undergone a wonderful evolution through the work and labours of chemists, who have shown how, by variation of the composition, the properties of glass may be altered in a most marvellous degree; and they have thereby made possible the construction of apparatus for the most diverse uses, prisms and lenses for lighthouses, microscopes, telescopes and other instruments, and so have contributed to the service of man and a knowledge of the universe.

But before we consider more fully the nature and properties of glass, there are one or two points of general importance to which it is necessary to direct attention.

We are all familiar with the statement that matter can exist in three states—the solid, liquid, and gaseous; and this

statement is familiarly illustrated by the substance water, which is well known in the three forms of ice, water, and steam. By elevation of the temperature, solid is made to pass into liquid, and liquid into gas, whereas by lowering the temperature the reverse series of changes is brought about.

At the present moment it is the change from solid to liquid, and more especially from liquid to solid, that demands our interest; and in using the term solid, I mean crystalline solid, and not amorphous solid. In a crystalline solid the particles are arranged in a definite geometrical form bounded by plane faces or surfaces, such as we see in the naturally occurring rock crystal, amethyst, etc.; whereas an amorphous solid does not naturally assume any definite shape, although it may, of course, be cut into definite forms in imitation of crystals. When a crystalline solid is heated it is found that it passes, *at a definite temperature*, known as its melting-point, from the solid to the liquid state, whereas an amorphous solid, like sealing wax for example, gradually loses its rigidity and possesses, therefore, no definite melting-point.

When a crystalline solid substance is heated, it is found that melting or liquefaction occurs as soon as the melting point is reached, and it has never yet been found possible to heat a crystalline solid to a temperature above its melting-point without such a change occurring. If, however, a liquid is cooled down, it is found quite generally that the temperature can be lowered below the normal freezing-point, or below the melting-point of the solid without any of the solid form being produced. We can, for example, with care, cool water to a temperature much

below 32° F. without any ice being formed, and liquids which are in this way cooled to below the normal freezing-point, are said to be *supercooled*. Such supercooled liquids appear to be quite stable—they can, apparently, be kept for any length of time unchanged—provided that all traces of the solid form are rigidly excluded. If, however, even a minute trace, even the ten thousand millionth part of a grain, of the solid substance—a particle which might dance as a mote in the sunbeam—is brought into contact with the supercooled liquid, the state of apparent equilibrium is upset, separation of the crystalline solid form begins, and the process goes on until all the liquid has passed into solid.[1] The process of crystallisation, however, does not take place at once throughout the whole mass of the liquid, but only those portions of liquid which are in contact with the solid crystallise out, and so we find the process of crystallisation gradually extending throughout the whole of the supercooled liquid. Moreover, the rate at which crystallisation takes place in a supercooled liquid depends on several factors; it depends on the nature of the substance itself, for it is found that different substances crystallise at different rates, and also on the purity of the substance, the rate of crystallisation being lowered by the presence of foreign substances. The velocity of crystallisation depends also on the degree of supercooling, and that is the factor on which I desire to lay most stress at present. The more a liquid is cooled below the normal freezing-point, the

[1] When the cooling is carried out slowly, it is found that substances differ greatly in the readiness with which they remain supercooled, but, in general, when a substance has been supercooled to a certain extent, crystallisation or separation of the solid in the crystalline form, takes place spontaneously, that is, without the previous addition of the solid form.

faster will solidification occur once it has been started. But this law, which is a perfectly general one, is subject to modification through the operation of another factor. We have already seen that the speed with which a chemical change takes place, depends on the temperature, the speed being all the greater the higher the temperature, and becoming less as the temperature is lowered. Similarly with the process of crystallisation. When crystallisation is started in a supercooled liquid, two opposing factors operate to affect the speed of crystallisation. At first the effect of supercooling is predominant, and so as the degree of supercooling is increased the rate of crystallisation also increases. But after a point, the effect of the lowering of temperature counterbalances the effect of the supercooling, the rate of crystallisation ceases to increase as the temperature is lowered, and in fact begins now to decrease. There is, therefore, a certain temperature, a certain degree of supercooling, at which the velocity of crystallisation is a maximum, and below which it becomes less and less; and, ultimately, it becomes practically equal to zero. The supercooled liquid no longer crystallises even when brought into contact with the crystalline solid.

But we know that as we cool down a liquid, it becomes more and more viscous, and at last it becomes so viscous that it does not "run" at all so far as ordinary observation can detect, and so we call it a solid. An *amorphous* solid is just such a supercooled liquid, a liquid cooled so far below its crystallising point that the rate of crystallisation is infinitely slow. In this way are formed, for example, the glassy lavas, or obsidians, by the rapid cooling of

molten lava, as well as ordinary glass with which we are so familiar.

When a supercooled liquid or "glass" is maintained at a temperature in the neighbourhood of the softening point, spontaneous crystallisation may set in, and thereby cause the glass to lose its transparent, vitreous character; the glass, it is said, *devitrifies*. Under certain circumstances, this may prove a source of much annoyance.

A substance which affords an excellent illustration of the behaviour which has just been discussed, is quartz or silica (an oxide of the element silicon), a substance which is very familiar to everyone. It occurs as the clear, glassy particles which form sea-sand, and which can also be readily distinguished in granite; coloured by certain impurities it forms the well-known ornamental stones, the Cairngorm and the amethyst, while in the pure colourless form it is known as rock crystal, which ordinarily crystallises in six-sided prisms ending in six-sided pyramids. It is largely employed for making spectacle glasses and optical instruments.

When this crystalline quartz is heated in the oxy-hydrogen blowpipe flame, or in a specially constructed electric furnace, to a temperature of about 3000° F., it melts to a colourless liquid; and when this liquid is cooled fairly rapidly, the quartz can be obtained as a clear, colourless, glassy mass—a supercooled liquid—which looks just like ordinary glass. This fused quartz, or quartz glass, possesses the exceedingly valuable property that it expands and contracts only very slightly with alteration of the temperature (its coefficient of expansion is less than

one-tenth that of glass), and for this reason it can, unlike ordinary glass, be rapidly heated or rapidly cooled without cracking. It can, for example, be heated red hot and then plunged into cold water, or when cold, it can be suddenly introduced into the blowpipe flame, or a wire enclosed within a tube of quartz glass may be heated to a bright red heat by means of an electric current while the tube is immersed in cold water, and the quartz glass remains in all cases uncracked. By reason of this property, quartz glass, formed into apparatus of various kinds, has come increasingly into use in recent years, more especially in cases where rapid changes of temperature are encountered. Although readily attacked by alkalies, it is very resistant to acids, except hydrofluoric acid.

When heated for some time to a temperature of about 2280° F., a temperature considerably below the melting-point of quartz, the glassy quartz passes into the crystalline form, it "devitrifies," and can then no longer withstand, as before, sudden changes of temperature.

Unlike fused quartz or silica glass, ordinary glass is not a single substance but a homogeneous mixture of substances. When quartz or silica, which occurs in great abundance as sea-sand—the grains of this consist of almost pure silica—is heated together with soda (sodium carbonate), the silica displaces the carbonic acid from the carbonate and a compound is obtained known as sodium silicate. When this is allowed to cool, it solidifies to a glassy material familiar to every one as *water-glass*, so called because of its solubility in water. A similar substance is obtained by fusing quartz with potash. If, instead of

heating sand or quartz with soda (or potash), only, one also adds other metallic oxides or carbonates, such as lime, or alumina, or oxide of lead, mixtures of silicates are obtained which solidify to glasses that do not dissolve in water, and constitute what we ordinarily call glass. Glass has, therefore, no definite composition, and by varying not only the constituents but also their relative amounts, glasses of various kinds and possessing very different properties can be prepared. All glasses, however, contain soda or potash.

Ordinary window glass, glass for table-ware and for general use, consists essentially of a mixture of the silicates of soda and of lime, although aluminium is also very frequently present in very small amount. The quality and appearance of the glass depend largely on the purity of the materials employed in its manufacture, and the principal source of the silica is a fine white sand found in various parts of England, but the purer sands of France and of Belgium are also laid under contribution. Such sand, mixed thoroughly with sodium carbonate[1] and pure white chalk or limestone, is melted in large fire-clay pots, placed in furnaces which are now generally heated by means of gas. At first the molten mass is almost opaque owing to the multitude of bubbles of carbonic acid gas which permeate it, but after a time these bubbles gradually escape, and a clear liquid is obtained. The desired articles can then be formed either by pouring the molten glass into moulds or by blowing. In the latter case, a quantity of molten glass is taken up on the end of a long metal tube, and by blowing through the tube, hollow

[1] Sulphate of soda is also largely employed in place of the carbonate.

articles of varied shape can, by the expert skill of the glass blower, be obtained. For the production of "sheet glass," used for windows, the molten glass is first blown into the form of a hollow cylinder, the ends of which are then cut off. By means of a diamond, this cylinder is then cut along its entire length and placed in a furnace heated to the softening point of the glass. The cylinder begins to unroll, and it is then flattened out into a sheet by means of a special instrument.

The surface of this glass is not quite plane, but is covered with slight depressions and bulgings, and in consequence of this, objects viewed through such glass are more or less distorted. To get rid of this defect, the sheet glass is sometimes ground and polished, as in the case of plate glass, and in this way one obtains what is known as "patent plate." Such glass is largely used for the framing of pictures.

After the sheet of glass or other article has been formed, it must be again heated to near its softening point and then placed in an "annealing" chamber where it can cool very slowly. The purpose of this is to get rid of the stresses which are set up in the rapidly cooled glass and which render the glass very liable to fall to pieces when scratched. This can be illustrated by what are known as Rupert's drops, obtained by dropping molten glass into hot oil, so that the glass is suddenly cooled. This glass is very hard, and can withstand even heavy blows with a hammer, but if the "tail" attached to the drop is broken, or if the glass be scratched with a file, the whole drop falls to a powder. Such hardened or toughened glass, produced by annealing glass in oil,

appears to have been known at least as early as the first century A.D., as the following incident, related by Petronius in that excellent satire, "Cena Trimalchionis," shows: "There was an artist who made glass vessels so tough and hard that they were no more to be broken than gold and silver ones: It so happen'd that the same person having made a very fine glass mug, fit for no man, as he thought, less than Cæsar himself, he went with his present to the Emperor, and had admittance; both the gift and the hand of the workman were commended, and the design of the giver accepted. This artist, that he might turn the admiration of the beholders into astonishment, and work himself the more into the Emperor's favour, begged the glass out of Cæsar's hand; and having received it, threw it with such a force against a paved floor, that the most solid and most firmest metal could not but have received some hurt thereby. Cæsar also was equally amazed and troubled at the action; but the other took up the mug from the ground, not broken but only a little bulg'd, as if the substance of metal had put on the likeness of glass; and therewith taking a hammer out of his pocket he hammer'd it as if it had been a brass kettle, and beat out the bruise: and now the fellow thought himself in heaven, in having, as he fancied, gotten the acquaintance of Cæsar, and the admiration of all mankind; but it fell out quite contrary to his expectation: Cæsar asking him if any one knew how to make this malleable glass but himself, and he answering in the negative, the emperor commanded his head to be struck off; 'For,' said he, 'if this art were once known, gold and silver will be of no more

esteem than dirt.'" In such fashion did Nero encourage and foster science.

By a systematic study of the influence of a large number of substances on the properties of glass, hundreds of different glasses have been produced and their physical and optical properties examined. Some of these glasses have proved themselves to be of the highest value and have made possible the construction of apparatus by which scientific knowledge and material well-being have been greatly promoted. Moreover, glasses possessing very different expansibilities with heat have also been produced, and by welding together combinations of these, glasses have been obtained which undergo little change of volume on heating and can withstand even considerable and sudden alterations of temperature without cracking.

The green colour so well known in the case of cheap bottle glass, and seen in practically all old window glass, is due to the presence of small amounts of iron derived from the impure materials, especially the sand, used in the manufacture of the glass. This green colour can be "corrected" by the addition of black oxide of manganese. The amethyst colour which is thereby produced neutralises the green due to the iron, and a white glass is obtained. The amethyst or purple colour due to the manganese becomes evident when such glass is exposed for a lengthened period to bright sunlight.

By fusing silica with a mixture of potash and red lead (oxide of lead), a lustrous glass with a high refractivity is obtained, and is known as "crystal." When cast in suitable moulds or, preferably, cut with a wheel and polished, it is much prized for vases and ornamental

dishes of different kinds. A still more lustrous glass can be obtained by replacing part of the silica in the crystal glass mixture by boric acid, and so giving rise to what is called generally a boro-silicate glass. By reason of its brilliant lustre and high refractive power, such a glass, when suitably cut, sparkles and flashes in a myriad colours. It is, therefore, largely employed under the name of "strass," or "paste," for counterfeiting diamonds, and, when suitably coloured, other gems as well.

The production of coloured or stained glass is easily effected by adding small quantities of suitable substances to the molten mixture of silicates. Thus, as we have already mentioned, addition of iron imparts a green colour to the glass, whereas the addition of manganese oxide colours the glass of an amethyst or purple shade. Salts of the metal uranium give to glass a yellowish-green fluorescence, and are much used in the production of fancy glass. With cobalt oxide the colour is deep blue, while with gold, a ruby red is obtained. Paste coloured blue with cobalt, or red with gold, is used to counterfeit the sapphire and the ruby. These counterfeit gems must not be confused with the artificially prepared sapphires and rubies to which reference was made previously (p. 51). They can readily be distinguished from the latter or from the naturally occurring gems by their much greater softness.

In most cases the colour in glass is due to the formation of coloured silicates, silicate of manganese, silicate of cobalt, etc.; but in the case of ruby glass, the colour is due to the presence of excessively minute particles of

metallic gold. When a small quantity of gold is added to molten glass it dissolves, much as sugar dissolves in water, and if the glass is rapidly cooled it is found to be white or to have only a very faint yellow tinge. If, however, this glass is re-heated, or if the molten glass is allowed to cool slowly, metallic gold begins to separate out in very minute particles. As the particles increase in size, the colour deepens more and more to a dark ruby red, and different shades can be obtained by careful regulation of the heating and cooling. The particles, however, are so minute that they are quite invisible not only to the naked eye, but even under a powerful microscope, and the gold is said to be in the *colloidal* state (Chap. X). If, however, too much gold is added, the metal may separate out in visible particles and so render the glass opaque.

Glass is also used in large quantities for the production of mirrors, which constitute a great advance on the polished metal mirrors of our forefathers. In order to avoid distortion, plate glass, the surface of which has been polished quite plane and smooth, must be used, and one side of this is "silvered." Formerly, this was effected by coating the glass with an amalgam of tin and mercury, but mercury is a very expensive metal and its use also involves the danger to the workman of mercurial poisoning. For the production of mirrors, therefore, this metal has been superseded by silver, the use of which is not only free from danger but allows also of a whiter reflecting surface being obtained. By adding caustic soda and ammonia to the solution of a silver salt, *e.g.* silver nitrate, a solution is obtained from which metallic silver can

readily be caused to separate out by the addition of certain substances, such as glucose. The surface of the mirror glass, previously well cleaned, is laid on the silver solution, and if the conditions are properly arranged, the silver separates out very slowly and forms a coherent and highly reflecting coating on the surface of the glass. Although silver is a fairly expensive metal, the amount used is so small that the silver required to coat even a large mirror would not cost more than a few pence. The silvering of the well-known "thermos" flasks is carried out in a similar manner.

When glass is heated for some time to a temperature just below the softening point, it devitrifies and becomes opaque owing to the crystallisation of the silicates present in the glass.

The use of carbonate of soda in the manufacture of glass brings that industry into the closest relations with a series of chemical industries in which this country was for long predominant, namely, the manufacture not only of soda itself but also of sulphuric acid, hydrochloric acid, chlorine, and bleaching powder.

Previous to the nineteenth century, the carbonate of soda required, more especially, for the manufacture of glass and of soap, to which we shall refer presently, was obtained mainly from the ash of marine plants which was prepared chiefly in Spain and sold under the name of *barilla*.[1] But the supply was scanty, and barely sufficient

[1] Sodium carbonate or soda has been known from remotest ages as forming a deposit on the shores of the soda-lakes of Egypt, and is obtained from that source at the present day. Formerly it was called "nitre," and

to meet the demand. There was, therefore, great need for an abundant source of cheap soda, and the Academy of Paris in 1775 offered a prize for a process of converting common salt, or chloride of sodium, of which there are such abundant supplies occurring naturally, into the carbonate of sodium or soda. This problem was solved by the French chemist Leblanc, in 1791. A factory for the manufacture of soda by the Leblanc process was started in 1793, but was confiscated by the Committee of Public Safety, and in 1806, filled with despair, the inventor of a process which has contributed so much to the comfort and well-being of the people by giving to them cheap glass and cheap soap, ended his days by his own hand. It was an inauspicious start for a great industry, but one, perhaps, not altogether out of keeping with the many vicissitudes through which it had afterwards to pass.

The process invented by Leblanc consists of several stages. Salt, first of all, is heated with sulphuric acid, whereby the chloride of sodium is converted into sulphate of sodium or "salt-cake," as it is called commercially. At the same time there are produced large quantities of hydrochloric acid gas. The salt-cake is then heated with a mixture of limestone (calcium carbonate), and coal, whereby the sulphate of soda is converted into carbonate of soda, which can then be extracted by means of water. A residue, consisting mainly of sulphide of lime, and known as alkali waste or soda waste, is left. For long,

by this name it is referred to in the Bible: "As he that taketh away a garment in cold weather, and as vinegar upon nitre, so is he that singeth songs to an heavy heart" (Proverbs xxv. 20). Soda, when acted on by vinegar (acetic acid), is decomposed with brisk effervescence due to the production of carbonic acid gas.

the accumulations of this soda waste were a source of much annoyance to the community (by reason of the evil-smelling gas, sulphuretted hydrogen, which they evolved), as well as a loss to the manufacturers. After many failures, however, a process was discovered whereby the sulphur present in the waste could be recovered, and the economy which was thereby effected enabled the Leblanc process to maintain itself, at least for a time, against the formidable rival by which, as we shall learn, it was assailed during the latter half of the century.

It was in England that the Leblanc process was chiefly worked, and there, together with the manufacture of sulphuric acid, the industry assumed very large proportions. But its history has been a checkered one. At first the hydrochloric acid gas which was evolved in the process was discharged into the air and became an intolerable nuisance, by reason of the fact that it destroyed all the vegetation in the neighbourhood of the works and rapidly corroded all ironwork. To still the outcry which was raised, more or less successful attempts were made to absorb the gas in water, in which it dissolves with great readiness. But if one trouble was thereby removed, a fresh one arose, and the soda manufacturers found themselves with large quantities of hydrochloric acid, for which there was scarcely any use, and which could not be run into the rivers as it would kill the fish. A way out of the difficulty, however, was at length discovered, and the hydrochloric acid which had been a source of annoyance to the community and of worry to the manufacturers, became a source of considerable profit. By heating the hydrochloric acid with black oxide of

manganese, and in other ways, *chlorine* is obtained, and this chlorine is a valuable bleaching and disinfecting agent. For convenience of transport and use, the chlorine is generally passed over slaked lime, which absorbs it and so gives rise to *bleaching powder*, or chloride of lime as it is popularly called. For this bleaching powder a great demand sprang up in the middle of last century, due to the development not only of the cotton but also of the paper industry, the raw materials for which required to be bleached before use. The production of hydrochloric acid played henceforward an important part in the success of the Leblanc process.

During the past fifty years, however, the Leblanc soda process has been faced with a competition before which it has almost entirely succumbed. In 1863 the Belgian chemist, Ernest Solvay, developed a process, the Solvay or ammonia-soda process, based on a reaction discovered by two English chemists, whereby soda can be produced more economically and in a purer form than by the Leblanc process. The process depends on the fact that when carbon dioxide is passed into a solution of common salt saturated with ammonia, bicarbonate of soda (used in the preparation of baking powder), is deposited. By heating the bicarbonate, carbon dioxide is driven off and the ordinary carbonate of soda is obtained. For a time the older process was able to maintain itself against its new rival, but although a quantity of soda is still manufactured by the Leblanc process, it is chiefly for the sake of the hydrochloric acid and the chlorine obtainable from it, that the manufacture is continued. The continuation of the process is also made more easy from the fact that the sulphate of

soda formed can be used, instead of the carbonate, for glass making. But yet "the old order changeth giving place to new," and the introduction of the electrolytic methods of making chlorine (owing, more especially, to the requirements of the dye industry), and caustic soda, which was formerly prepared entirely from the carbonate, seems seriously to menace the existence of the Leblanc process. But whatever may be the final result, the introduction of the Solvay process for the manufacture of soda, and of the "contact process" for the manufacture of sulphuric acid, has deprived this country of the predominance which she once possessed in the manufacture of these chemicals, and has enabled the other countries to become independent of us for their supplies. Of the 2,150,000 tons of soda produced in 1910, only 820,000 tons were produced in this country.

Another very large industry which is dependent on the use of soda is that of soap-making. Even at an early period, about the beginning of the Christian era, a material resembling our soft soap, and used largely as an ointment, was prepared by boiling fat with potashes; and although in later times the manufacture of soap developed considerably, it was not till early last century that it passed from being a handicraft carried on by rule of thumb, to an industry controlled by an exact knowledge of the properties of the materials used.

It has already been pointed out that the animal and vegetable fats and oils were shown by the French chemist, Chevreul, to be compounds of glycerine with different acids, which could be obtained by boiling the fats and oils with dilute sulphuric acid, or by treating them with superheated

steam. This process of *hydrolysis*, as it is called, or decomposition by water, can also be facilitated by caustic soda (sodium hydroxide), or caustic potash (potassium hydroxide), and the acid of the fat or oil then combines with the soda or the potash to form a sodium or potassium salt of the acid. This sodium or potassium salt of the fat or oil acid constitutes soap; and hence the process of decomposing a fat or oil by means of alkali is known as *saponification*.

For the manufacture of soap one cannot employ the carbonate of soda or of potash, but must first convert these into caustic soda or caustic potash. On adding slaked lime (calcium hydroxide), to the solution of the carbonate of soda or potash, a mutual decomposition takes place with formation of sodium or potassium hydroxide and calcium carbonate, and the latter, being insoluble, separates out. In this way the caustic lye of the soap-maker is generally prepared. The electrolytic preparation of caustic alkali is, however, assuming ever greater proportions, and may soon largely supersede the method which has just been described.

Although soap can be obtained by using either caustic soda or caustic potash, the nature of the product obtained in the two cases is different, the potash soaps being soft, the soda soaps hard.

The fats and oils used in soap-making are very varied in character. Formerly, animal tallow and olive oil were the chief raw materials employed, but, as has already been pointed out, the increased demand for margarine and other butter substitutes has driven the soap-maker to seek other sources of supply, and a number of different animal

and vegetable oils have now been forced into his service; these are either used as such, for the manufacture of soft soap, or are first "hardened" by the catalytic process referred to previously, for use in the manufacture of hard soap. By the admixture of different raw materials in varying proportions, soaps of different kinds and quality can be obtained; and in the proper blending of the raw materials lies the art of the soap-maker, an art which is now guided by careful scientific investigation.

In the manufacture of soft soap or potash soap, different animal or vegetable oils, *e.g.* linseed oil, cotton seed oil, soya-bean oil, are boiled with caustic potash. The oils are thereby decomposed with formation of glycerine and the oil acid, which combines with the potash to form soap. A thick paste is thus obtained which, owing to the presence of glycerine derived from the oil, does not dry up. Additions of water-glass and other "loading" materials are frequently made.

In the manufacture of hard soaps or soda soaps, caustic soda is gradually added to the fat or hardened oil, which is melted and kept stirred by means of steam. After the fat has become saponified, common salt is added, and this causes the paste of soap to separate out as a curdy mass on the surface of the liquid which contains not only the added salt and excess of alkali and various impurities, but also the glycerine of the fat. Although, at one time, this liquid used to be run to waste, it is now subjected to a process of distillation in special vacuum stills in order to recover the glycerine, for which there now exists a large demand for the manufacture of dynamite and other explosives. So valuable, indeed, is the glycerine that it

has been stated that the profit from the recovery of the glycerine is sometimes greater than that from the soap itself.

With the soap curd, after it has been suitably freed from the impurities present, there is incorporated any colouring matter or perfume which it may be desired to add. The soap is then placed in frames, allowed to dry and harden, cut into bars, and moulded into tablets.

Not infrequently this "genuine soap" is "filled" by the addition of other substances, such as carbonate of soda and water-glass. It is asserted that the soap is thereby hardened and its detergent power increased.

The familiar transparent soaps are obtained by dissolving pure soap in alcohol and then evaporating off the alcohol.

In the case of the cheaper varieties of soap, such as common yellow soap, the fat used is mixed with a quantity of rosin, which also undergoes a process of saponification to form a soap; and in this way a mixed fat and rosin soap is obtained.

Almost endless is the list of modern commercial soaps now offered for sale for special purposes, in which, with the genuine soap, there are incorporated disinfectants, medicaments of various kinds, scouring materials such as infusorial earth, bleaching materials such as perborates, etc.

The cleansing power of soap depends on its physical as well as on its chemical properties; and in this connection, its most important property is that it lowers the *surface tension* of water. What do we mean by this? Every one knows that when water is brushed over a greasy

surface, it does not form a continuous film wetting the surface, but breaks up into a number of separate drops, for all the world as if each little drop were surrounded by a thin elastic skin; and the force which keeps the water in the form of a drop is called the surface tension. If we reduce the surface tension sufficiently, if we reduce the strength of the imaginary elastic skin surrounding the drop, then the water will spread out over the greasy surface and wet it; and this lowering of the surface tension can be effected by dissolving a little soap in the water.[1] This property of soap of lowering the surface tension of water, is an important factor in its cleansing power, because it enables the water to wet and so to come into close contact with even a greasy surface. But there is another property of soap solutions which plays perhaps the most important part of all in the cleansing process. This is the property of emulsifying oils and fats. On shaking up any oil, pure olive oil, paraffin oil, etc., vigorously with water, it is found that a milky liquid is obtained owing to the oil being broken up into a large number of droplets. But this milky appearance is not permanent; in the course of a few minutes the droplets of oil run together to form larger drops, which then collect as a separate layer on the surface of the water. The milkiness thus disappears. If, however, the oil is shaken not with pure water but with water containing a little soap, the droplets into which the oil breaks up are much smaller (the emulsion appearing, in consequence,

[1] The effect described here will be familiar to every one who has interested himself in water-colour painting. To make the water-colour "take," a little ox-gall is added, when necessary, in order to reduce the surface tension of the water.

much whiter than before), and they do not run together and form a separate layer on standing. The oil is permanently emulsified. And this is what happens when soap is used in cleansing a greasy surface to which dust and other dirt so readily adhere; the film of grease is broken up owing to the emulsifying action of the soap solution, and the grease and dirt are then readily washed away. The removal of dirt is also facilitated in a purely mechanical way by the lather or foam which the soap-water forms, the production of lather being another result of the lowering of the surface tension of water.

Although the salts of the fat acids with soda and potash, the ordinary soaps, are soluble in water, the salts with lime and magnesia are insoluble. Consequently, when soap is brought into water containing salts of lime or magnesia, the soap is decomposed with production of the insoluble calcium or magnesium salt of the fat acid, which separates out as a scum. Thus—

Soluble soap (sodium stearate, etc.), and calcium bicarbonate (sulphate, etc.)

give

Sodium bicarbonate (sulphate, etc.), and insoluble soap (calcium stearate, etc.).

From its "feel" in washing such water is called "hard," and as the soap is decomposed, no lather can be obtained until sufficient soap has been added to combine with all the calcium and magnesium salts present. Since the bicarbonate or other salt of sodium which is formed,

does not lower the surface tension of water and has no power of emulsifying oils, the soap cannot exercise its proper cleansing function until after the removal of the calcium and magnesium salts.

Not only is hard water most wasteful of soap, but it may also be a source of annoyance, both domestic and industrial, owing to the separation out, in hot-water and steam boilers, of the salts of lime and magnesia. It is of importance, therefore, to get rid of or reduce the hardness.

When the hardness of water is due to the presence of bicarbonate of lime (formed by the action, on limestone or carbonate of lime, of the carbonic acid gas dissolved in rain water), it can be got rid of by boiling, and is therefore known as *temporary hardness*. On a large scale, the "softening" of the water can be effected by the addition of slaked lime in proper amount. The soluble bicarbonate is thereby converted into the carbonate which, being insoluble, separates out and is removed by filtration.

Hardness which is due to the presence of sulphate of lime or magnesia, cannot be removed by boiling, and is known as *permanent hardness*. It can be got rid of by the addition of carbonate of soda, or "washing soda," the lime or magnesia being thereby thrown out of solution as insoluble carbonates. Hence the use of washing soda in the laundry.

For industrial purposes, another process for softening hard water has recently been introduced, known as the *permutit* process. Permutit is an artificially prepared material formed by fusing together quartz, alumina and carbonate of soda. When hard water is filtered through

a layer of this material, the lime and magnesia are removed and the water is thereby rendered soft. When the permutit ceases to be effective, its activity can be restored by allowing it to remain in contact for some time with a solution of common salt.

CHAPTER IX

ELECTRICITY AND CHEMISTRY

IN a previous chapter it was sought to point out and to emphasise that a chemical reaction must no longer be considered as involving merely a transformation of material, but also a flow of energy; and it was also claimed that one of the chief characteristics of the scientific advance during the past hundred years has been the manner in which and the extent to which the different forms of energy have been transformed and utilised. In our study of the subject of combustion we had a glimpse into that branch of science, thermo-chemistry, which deals with the relations which exist between chemical energy and heat energy; and from the present chapter, it is hoped, the reader will gain some insight into the relationships which obtain between chemical energy and that other form of energy, the utilisation of which is so notable a feature of the past fifty years, electrical energy.

The birth of electro-chemistry, as this twin branch of science which deals with the relations between electricity and chemistry is called, may be dated from the time when, in 1791, the Italian physiologist, Galvani, observed the convulsive twitching of the muscle of a freshly dissected frog, each time the muscle and nerve were connected by two different metals. It was a humble birth, surely, for a

science which has revolutionised the world, which has made practicable the telegraph and telephone, and has supplied mankind with many materials both of ornament and of use.

If it is to Galvani that we owe the observation in which electro-chemistry found its birth, it is to his fellow-countryman, Alessandro Volta,[1] Professor of Physics in the University of Pavia, that the science owes its further development. Rightly interpreting the muscular contraction of the frog's leg as being due to the current of electricity which is produced whenever contact is made between two different metals separated from each other by a liquid conductor, Volta constructed an apparatus whereby a continuous current of electricity could be obtained through the transformation of chemical energy into electrical energy. When a strip of copper and a strip of zinc are partially immersed in a solution of sulphuric acid, Volta found that on connecting the free ends of the metals by means of a conducting wire, a current of electricity is obtained. By connecting a number of such cells together, so that the copper plate of one was joined to the zinc plate of the next, Volta built up a battery—the famous *couronne de tasses*, or crown of cups—with which effects of the most notable character were obtained; and the voltaic cell, as it was called, was the scientific sensation and curiosity of the end of the eighteenth and the beginning of the nineteenth century. Cells of a similar but more efficient character were constructed by

[1] The intimate connection of Volta with electricity is held in remembrance by the use of the term *volt* as the unit of pressure (or *voltage*) of an electric current.

others, and the effect of the electric current was tried on a great variety of substances, with the result that, under the guiding genius of Sir Humphry Davy, the alkali metals, sodium and potassium, were isolated for the first time in 1807, by passing a current of electricity through molten caustic soda and molten caustic potash.

These two metals, which are doubtless unfamiliar to most people, are silvery-white in colour, and very lustrous. When exposed to the air, however, they tarnish immediately, owing to the readiness with which they combine with the oxygen of the air. They are soft and of a cheese-like consistency, so that they can be readily cut with a knife. So great is their affinity for oxygen, that when brought into contact with water, they decompose it with great vigour, with production of hydrogen and formation of caustic soda and caustic potash. Such, in fact, is the vigour of the reaction that the hydrogen which is liberated, may become ignited and burn, with a yellow flame in the case of sodium, and a violet flame in the case of potassium. These metals find no application in ordinary life, but are used in considerable quantities in chemical manufactures.

Such was the beginning of man's triumphant success in transforming chemical into electrical, and electrical into chemical energy. Important as were the results obtained by the use of the voltaic cells, when regarded from the purely scientific point of view, the cost of working the cells was very considerable, and it was not, therefore, until the introduction of the dynamo (made possible by the scientific researches of Faraday), that the industrial application of electricity became

practicable. With the aid of the engineer and by means of the dynamo it has now become possible to obtain a cheap supply of electrical energy, more especially by harnessing the great waterfalls of the world and by the use of gas engines. The *couronne de tasses* of Volta has been replaced by the rows of humming dynamos which one sees, in our own country, for example, at the works of the British Aluminium Company at Kinlochleven in Argyllshire, at Niagara Falls, and in many other parts of the world; and in place of the few globules of metallic sodium which Sir Humphry Davy succeeded, with much difficulty, in isolating, that and many other substances are now produced by hundreds and thousands of tons in the electro-chemical factories of the world.

One of the earliest industrial uses to which electricity was put, was to the coating of cheaper with more expensive or more resistant metals, by a process known as *electro-plating*, a process which has been largely used from before the middle of last century. At the present day the process is largely applied to the plating of metals not only with silver and gold, but also with nickel, a metal much used on account of its white colour and its power of resisting atmospheric conditions without tarnishing.

In practice the process is comparatively simple, and consists in passing a current of electricity through a solution of a salt of the metal with which the article is to be plated; but in order that we may understand the process better, I would ask the reader to consider with me for a short time what is the nature of the liquids which conduct the electric current.

When one places in a vessel containing pure distilled

water, the ends of two wires which are connected with an electric lighting circuit and lamp (Fig. 12), the lamp remains dark. The electrical circuit is broken by the water which is a non-conductor of electricity. If to the water one adds cane sugar, glycerine, or alcohol, the lamp still gives forth no light, for the solutions of these substances do not conduct the electric current. But if one dissolves in the water even a very little common salt, or washing-soda, or hydrochloric acid (spirit of salt as it is frequently called), the lamp at once lights up, showing that

FIG. 12.

the flow of electricity is no longer interrupted by the liquid. In the same way other substances soluble in water may be tested, and it will be found that all substances can be divided into two classes, those that yield solutions which conduct electricity, and those that yield solutions which do not conduct electricity. Substances belonging to the former class are called *electrolytes*, substances belonging to the latter class, *non-electrolytes*. Sugar is a non-electrolyte; salt is an electrolyte. Similarly, all the substances known as *acids*, which have a sour taste and the property of turning red a blue solution of the vegetable colouring

matter called litmus; all the substances, also, known as *alkalies*, which have the opposite property of restoring the blue colour to solutions of litmus which have been reddened by acids; and lastly, all the substances known as *salts*, which are formed by the combination of acids and alkalies; all these substances, acids, alkalies, and salts, are electrolytes, and yield solutions which conduct the electric current.

When an electric current passes through the solution of an electrolyte, even the most superficial observation will teach us that a liquid conductor differs from a metallic one. In the latter case, no apparent change may take place, but in the former there is a very obvious decomposition of the conducting solution. This process of decomposition by an electric current is known as *electrolysis*. If one dips into a solution of copper sulphate, for example, two bright wires or plates of platinum which are connected with the poles of a battery, the solution of copper sulphate is decomposed and one sees that the surface of one of the *electrodes* (as the portions of the metallic conductor dipping into the solution are called), immediately becomes coated with a bright rose-coloured deposit of copper. This is the process used in electro-plating. In the case of solutions of sodium chloride, the sodium liberated at one of the electrodes decomposes the water with production of hydrogen gas, which can be seen rising in bubbles from the electrode, and the solution acquires an alkaline reaction, as is shown by the fact that it turns reddened litmus blue. At the other electrode, chlorine is set free and, dissolving in the water, yields a solution having

bleaching properties, as is shown by the fact that it discharges the colour of a litmus solution. Whenever, therefore, an electric current passes through a conducting solution, there is a movement of electrically charged matter through the liquid—charged particles of copper, or sodium, or chlorine, for example—and some of these particles move towards the one electrode, others towards the other electrode.

This conclusion was reached early last century by that great chemist, Michael Faraday, who called the electrically charged moving particles which thus conveyed the electricity through the solution, by the happily chosen Greek term *ions* (*i.e.* wanderers); and this term is still retained.

During a great part of last century there was much discussion as to the way in which the electric current was conveyed through a solution, and it was only in 1886 that a satisfactory explanation of the constitution of electrolytic solutions and of the mechanism of electrolysis was given by the Swedish physicist, Svante Arrhenius. Instead of assuming, as Faraday did, that the molecules of an electrolyte are broken up by the electric current—a view which has since been shown to be incorrect—Arrhenius assumed that the molecules of an electrolyte when dissolved in water, *break up or ionise of their own accord*, and the part-molecules which are formed are the electrically charged ions, some of these ions being charged positively, the others being charged negatively. These ions lead an independent existence in the solution and exhibit their own properties. Thus, sodium chloride, for example, when dissolved in water, ionises, not into ordinary sodium and chlorine, but into positively charged

sodium ions and negatively charged chlorine ions; and these ions lead an independent existence in the solution. Similarly, other salts, as well as acids and alkalies, undergo this process of ionisation or dissociation into ions, the metal part of the salt forming the positively charged ion, or *cation* as it is called, and the acid part forming the negatively charged ion, or *anion*. In the case of acids, hydrogen forms the cation, so that hydrochloric acid (HCl), for example, ionises into positively charged hydrogen ions, and negatively charged chlorine ions. It is, in fact, to the presence of hydrogen ions that the so-called acid properties are to be ascribed. In the case of alkalies, *e.g.* caustic soda or sodium hydroxide (NaOH), the anion is formed by the group of atoms OH, known as the hydroxyl group, so that sodium hydroxide ionises into positively charged sodium ions and negatively charged hydroxyl ions. It is to the presence of these hydroxyl ions that the general properties of alkalies are due.

In the light of the hypothesis of Arrhenius, the fact that addition of sodium chloride, or of any other salt, acid, or alkali to water, yields a solution which conducts the electric current, becomes readily intelligible. These solutions, according to the hypothesis, contain free, positively charged cations, and free, negatively charged anions. When, therefore, two electrodes are placed in the solution of an electrolyte and connected with an electric battery, the positively charged electrode (the *anode*) attracts the negatively charged ions, the anions; and the negatively charged electrode (the *cathode*) attracts the positively charged ions, the cations. These anions and cations move in opposite directions through the solution, and give up

their charges at the electrodes; they transport or convey the electricity through the solution, and it is this movement or procession of electrically charged particles that constitutes what we call the electric current in the solution.

This explanation of the passage of a current through a solution is not a mere speculation, not a mere phantasy, for it is easy to demonstrate not only that there is a movement of the ions through the solution, but also that the ions move with different velocities. There is a pretty experiment by which one can make this clear. Into the bend of a tube bent into the form of the letter U (Fig. 13), is placed a solution of potassium chloride to which sufficient gelatin has been added to make the liquid set to a jelly; and the solution is also coloured red by the addition of a substance called phenolphthalein and a little alkali. (Phenolphthalein is a colourless substance which yields a deep-red colour with alkalies, or solutions containing hydroxyl ions; and the red colour is again destroyed by addition of acids, or solutions containing hydrogen ions.) After the solution in the bend of the tube has set, a further quantity of the same coloured solution is poured into one limb of the

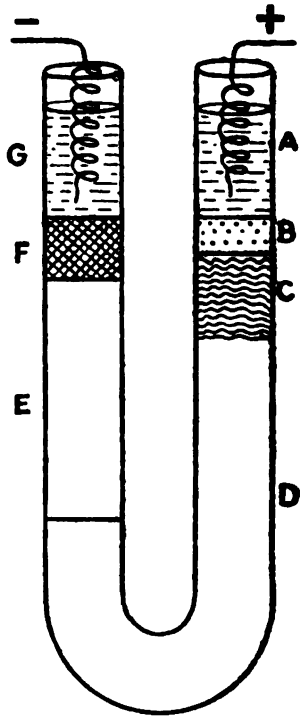


FIG. 13.—MIGRATION OF IONS.

tube (D), while into the other limb (E) is poured the same solution after it has been decolorised by the addition of the requisite amount of acid.

Above this colourless layer of gelatin is placed a quantity of a mixed solution of caustic potash (potassium hydroxide), and potassium chloride (G), while in the other limb of the tube is placed a mixed solution of hydrochloric acid and copper chloride (A). An electric current is now passed through the solutions in the tube, by placing a wire connected with the positive pole of a battery in the solution of hydrochloric acid and copper chloride; and a wire connected with the negative pole of the battery in the solution of caustic potash and potassium chloride. After the current has passed for some time it is found that the hydrogen ions (from the hydrochloric acid), moving from the positive towards the negative electrode, have decolorised the reddened phenolphthalein, and have produced, therefore, a colourless band (C) of a certain depth. The blue-coloured copper ions (from the copper chloride), which move in the same direction as the hydrogen ions but with a slower speed, follow on into the colourless band produced by the hydrogen ions, and give a blue colour to the gelatin (B). In the other limb of the tube, the hydroxyl ions (from the caustic potash), moving from the negative to the positive electrode, pass into the colourless gelatin and produce with the phenolphthalein there a band of red (F). This band is deeper than the blue band produced by the copper ions, but not so deep as that produced by the hydrogen ions, from which we conclude that the hydrogen ions move faster than the hydroxyl ions, and the latter faster than the copper ions.

But it is not only when in a state of solution that an electrolyte conducts the electric current; it conducts also when fused, or converted into the liquid state by heat. We conclude, therefore, that when fused an electrolyte dissociates into ions, and that the mechanism of electrolysis is essentially the same in the case of a fused electrolyte as in the case of an electrolyte in solution. This fact, as we shall see presently, is of the greatest importance for the practical applications of electricity to preparative chemistry.

Not only does the theory of Arrhenius afford an explanation of the process of electrolysis whereby electrical energy is transformed into chemical energy, or the potential energy of chemically reactive substances, but it helps us also to understand the reverse process of the transformation of chemical energy into electrical energy, as we see it occurring in the different voltaic cells.

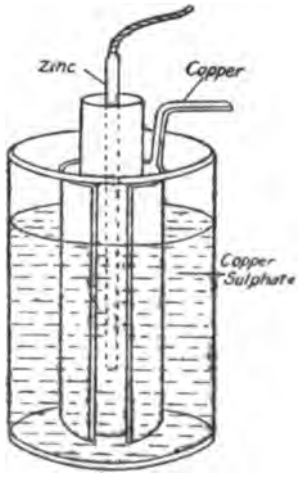


FIG. 14.—Daniell Cell.

One of the simplest of the voltaic cells is that known as the Daniell cell, which consists of an electrode of copper immersed in a solution of copper sulphate, and an electrode of zinc immersed in a solution of zinc sulphate. The latter solution is contained in a porous pot which prevents the mixing of the two solutions (Fig. 14).

When the copper electrode and the zinc electrode are connected by means of a conductor, an electric current flows through this conductor from the copper to the zinc. If an electric motor, for example, is inserted in the circuit, it will be caused to rotate, and so mechanical work can be done. What, then, is the source of this supply of energy which, either in the form of electrical energy, or in the form of the mechanical energy into which it is transformed, is given out by the Daniell cell?

When a strip of zinc is immersed in a solution of copper sulphate, copper is deposited on the zinc, and at the same time a corresponding amount of zinc passes into solution. The chemical change which takes place is therefore represented by the equation:

Zinc + copper sulphate = zinc sulphate + copper.

This is a reaction which takes place spontaneously; zinc and copper sulphate represent a system with a certain amount of potential energy, and it is capable, therefore, of doing work, of yielding energy. When the zinc is immersed in the solution of copper sulphate, the chemical energy is transformed into heat energy. How, then, can we obtain the transformation of the chemical energy into electrical energy? The answer is: by so arranging matters that the change represented by the above equation takes place by means of the electrically charged particles, the ions, which are formed when a salt is dissolved in water. In the Daniell cell, the solution of copper sulphate contains copper ions and sulphate ions, whereas the zinc sulphate solution contains zinc ions and sulphate ions. When the poles of the Daniell cell are connected by means

of a conductor, a movement of the ions in the solution takes place. The copper ions move towards the copper electrode, and the sulphate ions move in the opposite direction towards the zinc electrode. This movement of ions constitutes, as we have seen, the electric current in the cell. When the copper ions reach the copper electrode, they lose their positive charge, and are deposited as metallic copper on the electrode, while the positive electricity, to put it somewhat crudely, flows along the metallic conductor towards the zinc electrode. On the other hand, the negatively charged sulphate ions move towards the zinc electrode, where they give up their charge of negative electricity which neutralises the positive electricity flowing from the copper electrode. At the same time the zinc combines with the discharged sulphate ions to form zinc sulphate, which dissolves and again ionises into zinc ions and sulphate ions. The total result, therefore, is that copper ions pass into metallic copper at one electrode, while metallic zinc passes into zinc ions at the other electrode. In other words, instead of the reaction between zinc and copper sulphate taking place at one point by direct contact, whereby the chemical energy is converted into heat, the reaction in the Daniell cell takes place in two parts, at the two electrodes, and the chemical energy now appears in the form of electrical energy.

A better-known cell, widely employed for working telephones and electric bells, is the Leclanché cell. This very simple cell consists of a pot containing a solution of sal-ammoniac (ammonium chloride), in which are immersed a plate of graphite, packed in a porous pot with granules of graphite and black oxide of manganese (manganese

dioxide), and a zinc rod. The porous pot also contains a solution of sal-ammoniac. When the cell is in use, zinc passes into solution, while the hydrogen which is produced at the graphite plate is oxidised to water by the oxide of manganese, and so is prevented from forming a non-conducting layer on the electrode, and thereby stopping the current.[1] When the cell becomes exhausted, its activity can be renewed by replacing the spent liquid by a fresh solution of sal-ammoniac.

Although, as has been said, the much more efficient dynamo has superseded the voltaic cell as a source of electricity for industrial purposes, there is one cell which occupies an important place as an auxiliary to the dynamo. This is the lead accumulator, or storage cell. This cell consists of plates of lead and of brown oxide of lead, lead peroxide as it is called, immersed in a solution of sulphuric acid. On joining these two plates by means of a conductor, a current of electricity flows through the conductor from the lead peroxide plate to the lead plate. The chemical reaction which, in this case, yields the energy which is transformed into electricity, is the conversion of the lead and lead peroxide into lead sulphate; and when this change has taken place, no more electricity is given out; the cell is "run down" or "discharged." But this cell has the great advantage that it can be readily brought

[1] The ammonium chloride in solution gives rise to ammonium ions (consisting of the positively charged group of atoms NH_4), and to chloride ions or negatively charged chlorine atoms. When the cell is in action, the chloride ions move to the zinc pole and, on discharge, combine with the zinc to form zinc chloride which passes into solution; and the ammonium ions move to the graphite pole and there give up their positive charge. The discharged ammonium ions then react with the water with production of hydrogen.

back to its former condition, can be readily re-charged, by sending a current of electricity—obtained, say, from a dynamo—through the cell in the opposite direction to that of the current which the cell itself gives. In this way we convert electrical energy into potential, chemical energy; and in this form the energy is stored, and is available for use just when and where it is required. This lead storage cell is one which has now a multitude of uses, such as giving current for electric lighting on a large scale (as an auxiliary to the dynamo), or in portable hand-lamps; for driving motor cars or motor-boats; and in many other cases where a readily transported supply of energy is desired. As a competitor with the lead storage cell, much has, in recent years, been heard of what is generally known as the Edison cell. This cell consists of plates of iron and nickel hydroxide immersed in a solution of caustic potash, and has the advantage over the lead cell of less weight, and of being less harmed by careless or rough handling.

The application of electricity to chemical manufactures has produced an industrial revolution. Not only have electro-chemical processes more or less completely displaced the older chemical methods employed for the manufacture of such substances as caustic soda and of chlorine, or for the isolation of such metals as sodium, potassium, calcium, magnesium, and aluminium, but they have made possible also the discovery and economic production of many new substances of great value. One of the earliest applications of electricity we have seen was to the electro-plating of metals by a process of electrolysis. By this process metals can be obtained in a state of great

purity, and the method is now used for the refining of certain metals, more especially of copper. The crude copper, obtained by smelting its ores, contains a number of impurities, among which are silver and gold, sometimes in not inconsiderable quantities. This crude copper, cast into plates, is made the anode in a bath of copper sulphate solution, while a thin plate of pure copper is made the cathode. When the electric current is passed, copper is deposited in a pure state on the cathode, from which it can afterwards be readily stripped, whereas the copper of the anode passes into solution by combining with the sulphate ions which are discharged at the anode. Some of the impurities present in the copper may also dissolve and accumulate in the solution; other impurities, however, such as silver and gold, do not dissolve, but fall to the bottom of the bath as a slime or mud, known as the "anode mud," from which the valuable metals are extracted by suitable methods.

By this simple process, the purest commercial copper, so-called "electrolytic copper," is obtained, and is used largely for electrical purposes. The importance of pure copper in this connection is due to the fact that the conductivity of copper for electricity is greatly diminished even by small traces of impurity.

The electrolytic preparation of caustic soda and of chlorine, to which reference has already been made (p. 153), depends on the electrolysis of a solution of sodium chloride or common salt. As we have seen, chlorine is evolved at the positive electrode or anode, while the sodium ions, discharged at the cathode, decompose the water and yield hydrogen and a solution of caustic soda. By this process,

not only caustic soda but also chlorine and hydrogen can be economically produced on a large scale, and it might seem as if this electro-chemical process would speedily prove an irresistible competitor with the purely chemical method of manufacturing caustic soda (p. 154). And so it doubtless would, if it were not for the fact that the demand for chlorine and for hydrogen is at present rather limited. It is true that this electrolytic chlorine, generally liquefied and transported in iron cylinders, is used, in Germany alone, to the extent of some thousands of tons annually for the production of bromine as well as in connection with the manufacture of synthetic indigo; and for hydrogen, also, various uses can be found (*e.g.* in connection with the production of synthetic ammonia), but before any great development and extension of this electro-chemical process can take place, new fields of usefulness must be found for the chlorine and the hydrogen which are formed at the same time as the caustic soda.

Of the different substances produced with the aid of electricity, the best known is probably the metal aluminium. This is the most abundant of all the metallic elements in the world, but it occurs only in the form of compounds, in combination with other elements. So difficult is it to isolate the metal from its compounds by purely chemical methods, that it was not till 1845 that the metal was obtained in the compact form. And it was then merely a chemical curiosity; for any general or industrial application, its cost was prohibitive. It is, in fact, only during the past thirty years, that it has become possible, by the application of an electrolytic method, to produce the metal at a reasonable price. The isolation of the metal is

effected by the electrolysis of a solution of purified bauxite or oxide of aluminium in molten cryolite (a naturally occurring compound of aluminium with fluorine and sodium, mainly obtained from Greenland), and the entire world's production of the metal is now obtained by this means. For the electrolysis, an iron bath, lined with carbon, is used and forms the cathode, while large carbon rods dipping into the molten mixture form the anode. As the current of electricity passes through the molten mass, aluminium separates out at the cathode and collects in the liquid form at the bottom of the bath, whence it can be run off from time to time. At the anode, the oxygen which is liberated combines with the carbon electrode, producing the poisonous gas carbon monoxide, which may either escape as such or burn to form carbon dioxide.

The production of aluminium is now carried on in a number of countries, more especially in those where an abundant water-power is available. In this country the isolation of the metal is carried out by the British Aluminium Company at Kinlochleven, in the north of Argyllshire. To obtain the power necessary to drive the dynamos for the generation of the electricity required, a great storage reservoir has been created, high up among the mountains, by building a great barrage across the valley of the River Leven.[1] From this reservoir the water is led through an aqueduct, three and a half miles in length, to a penstock, situated on a shoulder of the mountain, 900 feet above the factory and more than a

[1] The dam is over 1000 yards in length, with a maximum height of about 86 feet, and is capable of impounding twenty thousand million gallons of water.

mile distant from it; and from this point the water rushes down to the turbines, through pipes of more than a yard in diameter.

Although the great expectations which were at one time entertained with regard to this metal have not been entirely fulfilled, aluminium, nevertheless, now occupies a permanent and ever-growing place in our modern life. Not only is it largely employed for articles of ornament and of domestic use, and where lightness and portability are of importance, but it is being increasingly used as a conductor of electricity and, as we have seen, for the production, by the "thermit" process, of high temperatures and for the isolation of certain metals. Moreover, some of the defects which militated against a more widespread use of the metal, its low tensile strength and softness for example, can be partly removed by admixture with other metals, some of the alloys formed possessing properties of great value. With copper, aluminium yields a bronze, *aluminium bronze*, of great hardness and high tensile strength, which is practically not corrodible by sea-water; and when added to brass, aluminium greatly increases the tenacity of that alloy. With the metal magnesium, aluminium forms a valuable alloy called *magnalium* (containing from 1–2 per cent of magnesium), which is even lighter than aluminium itself and is equal to brass in strength. The metal *magnesium*, used in the production of this alloy, is a grey-coloured metal, which burns with a very bright and photographically active light, and is consequently used in the preparation of "flash-lights." It is obtained by the electrolysis of fused chloride of magnesium.

But it is not only of the decomposing action of electricity, in the process of electrolysis, that use is made. From the everyday use of electricity for heating and lighting purposes, all are familiar with the fact that heat is produced by the passage of electricity through a conductor which offers a certain amount of resistance to the current; and by increasing the strength of the current, the temperature may be raised to any point we please, limited only by the melting or vaporising of the conducting material. We have already seen, also, that by means of the electric arc, electrical energy is transformed into heat energy, and that the very high temperature of 5000°–6000° F. can in that way be obtained. A most powerful instrument has, therefore, been put into the hands of the chemist, and by its means he has been enabled not only to advance to a fuller knowledge of substances and materials already known, but also to prepare others which were hitherto unknown.

Of the utility of electricity applied to the production of high temperatures, we have already had some examples in the direct combination of atmospheric nitrogen and oxygen, and in the manufacture of calcium carbide and calcium cyanamide. Fused quartz or silica glass, with the valuable properties of which we have also become acquainted, is also produced by the fusion of quartz sand in specially constructed, electrically heated furnaces; and the high temperatures which can now be produced economically by means of electricity, are made use of in the preparation of the substance phosphorus, which is so largely used in connection, for example, with the manufacture of matches.

As a direct result of the successful application of electricity to the production of high temperatures, we owe the very valuable material known as *carborundum*, a compound of carbon and silicon, discovered by the American chemist, Dr. Edward G. Acheson, in 1891. By heating a mixture of coke (carbon) and sand (oxide of silicon) to a high temperature in an electric furnace (Fig. 15), oxygen is removed by the carbon from its

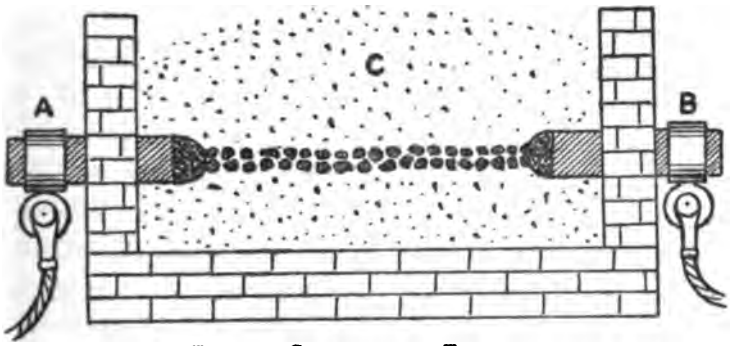


FIG. 15.—CARBORUNDUM FURNACE.

A core of granular graphite is raised to a white heat by a powerful current of electricity which passes between the graphite terminals A and B. At the high temperature which is thereby produced, the carbon and sand of the surrounding mixture, C, react with formation of carborundum.

combination with silicon, and the latter then combines with the excess carbon to form the crystalline substance, carborundum, the hardness of which approaches that of the diamond. This material is now produced in large quantities and used as a grinding or abrasive material, as well as for incorporating in the surface layer of concrete pavements, stairs, etc. By reason of its very refractory character (it will withstand a temperature of 4000° F. without undergoing change), it is also used

for the protection of furnace walls, and for other heat-resisting purposes.

Another very valuable abrasive and refractory material of which mention may be made, is *alundum* (alumina or aluminium oxide), obtained by fusing purified bauxite in an electric furnace.

From the manufacture of carborundum there resulted still another discovery of much importance, the discovery of a method of making *artificial graphite*. Until about twenty years ago, graphite, a crystalline form of carbon familiar under the names of plumbago and black lead (although it contains no lead at all), was known only as a naturally occurring mineral. But during the process of manufacture of carborundum it was found that the ends of the rods of gas carbon (a very dense amorphous variety of carbon formed in gas retorts), by which the electric current was carried into the furnace, were converted, by the high temperature to which they were exposed, into graphite; and, moreover, carborundum itself, when heated to a sufficiently high temperature, decomposes with production of graphite. In this way there was initiated a new industry, the manufacture of artificial graphite, which has undergone so great a development that artificial graphite is now produced at Niagara Falls at the rate of 15,000,000 lbs. annually.

For the production of Acheson graphite, amorphous carbon (anthracite coal, coke, etc.), mixed with a small amount of oxide of iron, alumina, or silica, is heated to a high temperature (5000°–6000° F.) in an electric furnace of the same type as the carborundum furnace. At this high temperature the iron, alumina, or silica which was

added, is converted into vapour, and the amorphous carbon passes into graphite. The silica and metal oxides added to the coke act as catalysts and accelerate the conversion of amorphous carbon into crystalline graphite; in their absence the change takes place only with difficulty.

To obtain graphite rods, plates, etc., finely-ground coke, to which a small quantity of oxide of iron is added, is mixed into a thick paste with pitch or tar. After this paste has been moulded under high pressure it is heated in the electric furnace, and the amorphous carbon thereby converted into graphite.

This artificial graphite, which is superior to the natural mineral by reason of its greater purity and uniformity, is employed in a variety of ways. For electrical purposes, whether for use in the construction of dry cells or as electrodes in electro-chemical processes, it is greatly superior to the dense gas carbon formerly employed, on account of its greater electrical conductivity and its mechanical properties; and to another very important use to which artificial graphite is put, reference will be made in the following chapter.

Some one has said, "Nature's storehouse is man's benefactor, and no gift from it renders greater service than the waters of the earth"; and in the recent developments of electro-chemistry we have seen how Nature's gift has proved of service to man. Although the harnessing of the great rivers and waterfalls of the world is due to the engineer, and was made possible only by the advances in mechanical and electrical engineering of last century, the *utilisation* of the enormous amounts of energy contained

in the flowing waters of the earth, the rendering available of which represents so much real gain, so much real progress for the benefit of mankind, is due chiefly to the labours of the chemist. The combined achievement is one that may well fill the mind with wonder; and even the most careless tourist cannot but be profoundly impressed if, after gazing, shall we say, on the majestic, down-leaping of the mighty waters of Niagara, he passes into the power stations near by, where the turbines and humming dynamos, working in obedience to the will of man, without the smoke and dirt and clatter of the ordinary factory, are transforming the energy of the rushing river into the energy of electricity which, in the adjacent factories, is then made to contribute to the material well-being of man and the advance of civilisation.

CHAPTER X

THE COLLOIDAL STATE

WHEN one brings sugar, salt, washing-soda, and many other common and familiar substances into contact with water, the solid substance, if present in not too large amount, disappears; it *dissolves*, and a clear liquid is obtained which we call a solution. For long chemists and physicists have puzzled over this process, and they puzzle even yet; for while some consider the production of a solution to be due to the chemical combination of the dissolved substance, or *solute*, with the solvent, others see in the process nothing more than the mechanical intermingling of the molecules of the constituents of the solution. Doubtless there is truth in both these views, but even if combination does take place we must not regard the solution as a whole as being a compound of water with the sugar, salt, or whichever other substance is taken. A compound is characterised, as we have already seen, by the fact that its composition is perfectly definite and constant, and cannot be altered by adding more or less of one of the constituents. The composition of a solution, however, can be altered as we please; the proportions in which the solid and the liquid are present in the solution may be varied, in some cases varied very

greatly, so that we obtain solutions of different strength or concentration. Even if chemical combination does take place, it appears to do so only to a limited extent, and is accompanied by a mechanical intermingling of the molecules. We may, therefore, regard a solution as being merely a homogeneous mixture in which the molecules of the dissolved substance or solute, combined, it may be, with a limited number of solvent molecules, are uniformly distributed throughout and among the molecules of the water, or other liquid which acts as the solvent. It is a homogeneous mixture of variable composition.

If, however, we leave on one side the question of the nature of the solution process, and consider merely the properties of the solution produced, one of the most remarkable facts established by the modern investigation of solutions is the very close analogy which exists between a substance in solution and a gas. For our present purpose it is sufficient to refer to only one feature of the analogy, the property of *diffusion*.

To account for the properties of gases there was developed, about the middle of last century, a theory known as the kinetic theory of gases, which was based on the hypothesis that the molecules of a gas are in perpetual and rapid motion, darting about in straight lines with the speed of something like a mile a second, colliding ever and anon, some eighteen thousand million times a second, with other molecules, and pursuing, therefore, as the result of these collisions, a very zigzag course. It is by virtue of this motion inherent in the molecules that a gas can distribute itself or diffuse rapidly throughout a room, or can fill completely the space, howso large that

space may be, which is offered to it. In the case of liquids the same inherent motion of the molecules, and therefore the same power of diffusion, exists; but the process now takes place more slowly, for the molecules of the liquid are packed more closely together, and the mutual collisions are therefore more frequent. The forward progress of a molecule is therefore very slow, like that of a man who might try to pass through a dense and jostling crowd. But still diffusion does take place, as we can easily satisfy ourselves by gently pouring a layer of pure water on to a solution of some strongly coloured substance, such as blue-stone (copper sulphate) or bichromate of potash. After some time we shall find that the coloured substance has diffused upwards some distance into the water. The experiment may be made more easily by dissolving in the water sufficient gelatin to make a firm jelly, and then placing a piece of this jelly in the coloured solution. After a few hours it will be found that the coloured substance has penetrated some distance into the jelly.

Even when the solution is separated from the pure water by a membrane of parchment paper or by an animal membrane (*e.g.* pig's bladder), diffusion takes place just the same, as we can show by enclosing the solution of copper sulphate in a tube of parchment paper which we then immerse in water. Very soon we shall be able to detect the presence of the copper sulphate in the water outside the membrane.

During the sixties of last century this diffusion of dissolved substances through a parchment or animal membrane was studied more fully by Thomas Graham, a native of Glasgow, who later became a Professor of Chemistry in

London, and Master of the Mint. As a result of his investigation, Graham found that although certain substances pass through a membrane of parchment paper, other substances do not do so. Since the substances, *e.g.* sugar or salt, which could pass through this membrane, were such as generally crystallise well, whereas those which would not pass through, *e.g.* starch, gelatin, glue, were amorphous and non-crystallisable, Graham divided substances into the two classes, crystalloids and colloids (from the Greek κόλλα, glue), and this distinction was one which was long maintained. From a practical point of view, in any case, this distinction was of importance, for, as Graham showed, if a mixture of crystalloids and colloids is placed in a parchment cell and immersed in water, the crystalloids, but not the colloids, diffuse out into the water. In this way a separation of crystalloid from colloid can be effected by a process to which Graham gave the name of *dialysis*, a process used universally at the present day for the preparation of colloids free from crystalloids.

Appropriate as Graham's classification of substances appeared at the time, recent investigation has shown that it cannot any longer be retained. The terms colloid and crystalloid can now no longer be employed to connote definite and different *kinds* of substances, but only different *states* of matter; for not only have substances such as albumin and gelatin, which Graham regarded as distinctively colloid, been obtained in the crystalline form, but even such definitely crystalloid substances as common salt have been obtained in the colloidal state. But language changes slowly, and although, through the advance of knowledge, a term may acquire a different

signification, the term itself persists. And so one still speaks of colloid substances, but means thereby substances in the colloidal state, which may be defined as a state in which one substance forms with another mixtures which although they may appear homogeneous to the eye, even when aided by the microscope, are nevertheless heterogeneous, the diverse colloid particles having a magnitude greater than molecular. These apparently homogeneous, but in reality heterogeneous mixtures, are called colloidal solutions, or simply colloidal *sols*.

But it may be asked, how can we assert that these colloidal sols are heterogeneous mixtures when we cannot detect any want of uniformity even with the aid of the microscope? The answer is, that even if we cannot see the particles themselves we can detect their presence, and the manner in which this can be done was shown long ago by Tyndall. Regard the air of a room bathed in a uniform light. Can you see any particles there? No. But darken the room and let a ray of sunlight pass through a hole or chink in the shutters, and what do you see? A diffused light, the sunbeam made visible, in which the larger dust particles are seen to dance and swirl; the diffused light also being due to particles which are large enough to reflect and scatter the waves of light, although too small to be seen as separate individuals by the eye. So also, by means of this "Tyndall phenomenon," as it is called, the presence of particles in a colloidal sol can be detected. Pass a beam of light through pure water or through a solution of salt, the path of the beam is invisible; the liquid is "optically empty."[1] But pass the

[1] Owing to the presence of floating particles even in filtered water, the

beam through a colloidal sol, and the path of the beam is traced by a diffused light, like the sunbeam in a darkened room.

From this "Tyndall phenomenon," then, we learn that particles which may be too small to be seen in the ordinary way, may be detected if only the light reflected or dispersed by the particles, and not the direct rays from the source of light, are allowed to enter the eye. And it is clear that if, instead of the unaided eye, we employ a microscope to examine the scattered light, we shall still further extend our range of vision, and be able to detect, although not actually to see in their own shape and colour, particles which are much smaller than can be seen when the microscope is used in the ordinary way. Through the recognition of this principle there has been devised, in recent years, an arrangement known as the *ultra-microscope*, by means of which not only the heterogeneity can be detected, but also the number of particles in a given volume of the sol determined. A powerful beam of light, instead of being directed into the microscope through the liquid to be examined, is sent horizontally into the liquid, at right angles to the line of vision through the microscope (Fig. 16). If the liquid under examination is optically empty, the field of view in the microscope will appear quite dark; but if particles are present in the liquid, the light will be reflected and dispersed, and the minute points of light thus produced will stand out, against a dark background, in the field of view of the microscope.

And how large are those particles which are thus

"Tyndall phenomenon" will be observed with ordinary pure water. Special precautions must be adopted to free the water from all suspended particles.

detected in the apparently homogeneous colloidal sols? With the aid of even the most powerful microscope, the smallest particle that can be seen by the ordinary method, must have a diameter of not less than about one sixty-thousandth part of an inch; but by means of the ultra-microscope, particles one-eightieth of this size, with a diameter of about one five-millionth of an inch, can be

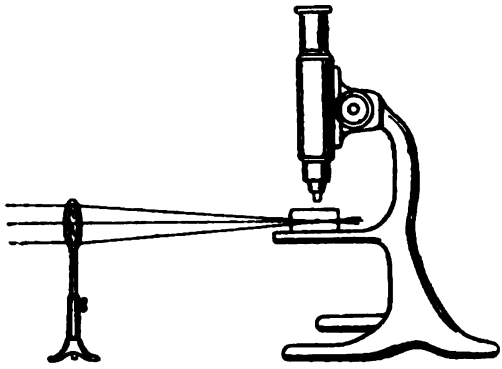


FIG. 16.—ULTRA-MICROSCOPE.

detected. This, however, is still about thirty times greater than the diameter of the hydrogen molecule.

From the investigations carried out by means of the ultra-microscope, it is found that colloidal sols may contain particles of very different size, even in the case of the same substance, and there is every reason to believe that there exist in some at least of the sols particles which are smaller than can be detected by the ultra-microscope, although they are of greater than molecular dimensions. In short, there appears to be no sharp division between colloidal sols and true solutions, and it is possible to pass gradually and without break from one to the other.

And now let us see what are the main properties of this colloidal state.

If we dissolve, say, two or three parts of gelatin in a hundred parts of water,[1] we obtain a rather viscous liquid which, on being cooled down, "sets" to a firm jelly; and this jelly, on being heated, melts again to a viscous liquid. In this case, therefore, which is familiar to every one, a reversible change from the liquid or sol state to the state of a more or less rigid jelly, known as a *gel*, can be effected. If we add small quantities of salts to this gelatin sol, there will be no apparent change, but it will be found that the temperature at which gelation, or the change from the liquid sol to the rigid gel takes place, is altered; it is raised or lowered according to the salt taken.

But a very different behaviour is found in the case, say, of the colloidal sol of sulphide of arsenic (arsenious sulphide), obtained by passing sulphuretted hydrogen into a solution of white arsenic (oxide of arsenic). This is a clear, yellow-coloured liquid which can be passed unchanged through filtering paper (a finely porous, unglazed paper); it is as mobile as water itself, not viscous like the gelatin sol; and it does not set to a gel when cooled down. The water, indeed, may be frozen to ice, but, on thawing the ice, the sol of arsenic sulphide is obtained as before. The arsenic sulphide sol, also, differs very markedly from the gelatin sol in its behaviour towards salts. By the addition even of small amounts

[1] The gelatin is first allowed to remain in contact with cold water until it has swelled up and become soft. It is then warmed up with water, or is placed in hot water.

of different salts, the sulphide of arsenic is caused to separate out as an insoluble yellow solid.

This marked difference in the behaviour of colloidal solutions of gelatin and of sulphide of arsenic, which may be taken as typical of two classes of colloids, is traceable to a distinct difference in the nature of the two sols. In the case of the gelatin sol, we have a mixture of two liquids; it is comparable, therefore, with an emulsion, say, of oil and water, and is, for that reason, called an *emulsoid*. When jelly formation takes place, a honey-comb structure is produced due to the separation of the sol into two parts. One part, forming the walls of the "honey-comb," consists chiefly of the colloid (gelatin) with a little water; the other part, filling the cells of the "honey-comb," consists chiefly of water with a little of the colloid. When such an emulsoid colloid is examined by means of the ultra-microscope, no definite particles are seen, but only a general diffused light.

In the case of the colloidal solution of sulphide of arsenic, however, we have a mixture, not of two liquids, but of a solid (arsenic sulphide) and a liquid (water); and examination with the ultra-microscope shows that the arsenic sulphide is present in the form of minute particles, too small to be seen by the eye. Such a colloidal sol is therefore comparable with an ordinary suspension, such as muddy water, and is therefore called a *suspensoid* colloid.

One of the most marked characteristics of suspensoid colloids, and one which we have already seen demonstrated in the case of sulphide of arsenic, is found in the fact that addition of salts, or, speaking generally, of electrolytes,

brings about, with varying degrees of effectiveness, the separation or precipitation of the colloid in an insoluble form. A similar behaviour is found in the case of ordinary fine suspensions, *e.g.* of clay in water, and this is sometimes of considerable geological or geographical importance. Thus, the sedimentation of finely divided, water-borne clay is markedly influenced by the purity of the water transporting it, taking place more rapidly when salts are present than when they are absent. This, indeed, is one reason for the rapid deposition of river mud on mixing with sea-water, and for the consequent silting up of river mouths and the formation of deltas, such as has taken place at the mouth of the Nile.

But this precipitation of suspensoid colloids and the sedimentation of fine suspensions by electrolytes, is counteracted more or less effectively by the presence of emulsoid colloids, *e.g.* gelatin or albumin, so that, in their presence, a much larger amount of electrolyte is necessary to produce precipitation or sedimentation. The emulsoid colloids exert a "protective" action, and the suspension or the suspensoid colloid is rendered much more stable. Indeed, so stable may the colloid become that the colloidal sol may even be evaporated to dryness without destroying the colloidal state; on treating the dried solid with water, it passes back again into the state of a colloidal sol. Such colloid sols, *e.g.* colloid silver or collargol, now find important uses in medical practice as powerful bactericides.

In the manufacture of photographic plates, prepared by coating plates with gelatin containing a fine suspension of silver bromide, we have an important industrial application of the protective action of emulsoid colloids. If a

solution of potassium bromide is added to a solution of silver nitrate, silver bromide is formed and separates out as an insoluble curd, quite unsuitable, on account of its coarseness, for photographic purposes. But if gelatin is first dissolved in the solutions of potassium bromide and of silver nitrate, no curdy precipitate but only a uniform colloidal suspension of very fine particles of silver bromide is obtained on mixing the solutions.

The protective action of emulsoid colloids and the precipitating action of salts, are excellently illustrated, also, on a large scale in nature. Some of the great rivers of the world, like the Mississippi and the storied Nile, whose turbid waters have from time immemorial carried in their bosom the promise of bountiful harvests, are always muddy, whereas other rivers which are even more swiftly flowing, like the Ohio, are, except in times of flood, perfectly clear. In the case of the first two rivers there is much colloidal organic matter washed into them by which the clay and soil are retained in a state of fine suspension; and it is only when the rivers reach the salt waters of the sea that the suspended matter is precipitated with the production of river bars and deltas. In the case of the River Ohio, however, the water remains clear owing to the absence of colloidal organic matter and the presence of lime and other salts.

Even when a colloid has separated out from solution in the solid form, it can, in many cases, be brought back into colloidal solution again, or be "peptised," as it is said, by small quantities of various substances. A very interesting illustration of this behaviour, and one which is of the greatest importance in our everyday

life, is seen in the plastic properties of clay. Clay is a hydrated silicate of alumina which possesses the property, in its normal condition, of forming, more or less readily, with water, a fine suspension or suspensoid colloid. On this property depends what is called the plasticity of clay, and just as the presence of certain substances renders the clay suspension more stable, so also certain substances facilitate the passage of the precipitated clay into the state of colloidal suspension; they render the clay more plastic.

Everyone is familiar with the story of how Pharaoh commanded his taskmasters to increase the burdens laid on the Israelites by withholding from them straw wherewith to make bricks; and doubtless many have wondered wherein the hardship lay. By most people, probably, the view has been held that the straw was added as a binding material, much as hair is used in mortar; but such an explanation is scarcely satisfying when it is remembered that the straw fibre is a very weak one, and when we read, moreover, that when straw could not be obtained, stubble was used. Another explanation may therefore be offered.

About fourteen years ago it was found by Dr. E. G. Acheson, to whom we owe the discovery of carborundum and the process of making artificial graphite, that when clay is mixed with a dilute solution of tannin, it becomes much more plastic, and the strength of the dried brick is, moreover, greatly increased. Although straw does not contain tannin, it was found that when straw is treated with water, the extract obtained has the same action on clay as tannin has, the plasticity of the clay and the hardness of the brick being greatly increased. It seems therefore a plausible view that the straw was used, not for

the purpose of binding the clay, but for the purpose of rendering the clay more plastic; and the particular burden imposed on the Israelites would therefore consist in their having to make bricks with a less plastic and, consequently, more difficultly worked material. In allusion to this Dr. Acheson gave to the clay which had been rendered more plastic by the addition of tannin, the name of "Egyptianised clay."

The property of tannin of facilitating the production of an ultra-microscopic or colloidal suspension, has also been applied to the production of a colloidal suspension of graphite for use as a lubricant. By means of the very high temperature which can be obtained in the electric furnace, Dr. Acheson was able to prepare from anthracite coal a form of graphite which could be ground to a fine powder. Such graphite, however, when shaken with water or oil, yields a suspension from which the graphite soon settles out; but if the graphite is first treated with a solution of tannin, it becomes "deflocculated," as it was said, and forms a colloidal suspension which can be kept indefinitely without showing any tendency to separate out. The colloidal suspension of "Deflocculated Acheson Graphite" in water is known as *aquadag*,[1] or *water-dag*, and is used as a lubricant for metal-cutting tools. By filtering the aquadag under pressure through thin films of rubber, the colloidal graphite can be obtained as a paste. When this is mixed with oil, a colloidal suspension known as *oildag* is obtained which is much more efficient as a lubricant than oil alone.

[1] The termination *dag* is derived from the initial letters of Deflocculated Acheson Graphite.

These colloidal suspensions of graphite are so fine that the graphite particles will pass through the finest filter paper. On adding salts, however, the graphite is flocculated, as we have seen is the case with colloidal suspensions of sulphide of arsenic and of clay, and the graphite is now retained by filter paper, and separates as a sediment on standing.

Although we have seen that various differences exist in the nature and behaviour of the two classes of colloidal solutions, the emulsoid and the suspensoid, there is one respect in which the two classes resemble each other, namely, in the relatively large extent of surface exposed by a given amount of colloid. This large development of surface is due, in the one case, to the honey-comb or sponge-like structure of the colloid sol; and, in the other case, to the minute size of the particles, for the more a given mass of matter is subdivided, the greater becomes the extent of surface exposed. To the existence of this highly developed surface, one of the most characteristic and important actions of colloids, namely, the removal of substances from solution, is due. When, for example, a colloidal solution of ferric hydroxide, the so-called dialysed iron of the pharmacist, is shaken with a dilute solution of white arsenic, a large proportion, it may be practically the whole, of the arsenic is removed from solution and collected or *adsorbed* on the surface of the colloid, and it is to this property of colloids that the use of dialysed iron as an antidote in arsenical poisoning is due.

This adsorbing action of a large surface depends on the fact that the concentration of a dissolved substance in

the surface layer of a solution is different from, and frequently greater than, what it is in the body of the solution. When the concentration of the dissolved substance in the boundary layer is greater than in the body of the solution, the dissolved substance becomes concentrated in the layer of solution in contact with the solid, and this film of concentrated solution remains adhering to the surface of the solid when the rest of the liquid is poured off. Herein we find, also, the explanation of the action of the very porous material, charcoal, in removing dissolved colouring matter from solution, a property which finds a very important application for the removal of the colour from molasses in sugar refining.

But the special and peculiar behaviour of colloids depends not only on their power of surface adsorption, but also on the fact that the colloid particles are electrically charged. In some cases, *e.g.* ferric hydroxide and aluminium hydroxide, the colloid is positively charged, but in most cases, it is negatively charged.

The existence of such an electric charge can readily be demonstrated with a colloidal solution of sulphide of arsenic. If this is placed in a U-shaped tube, and if we then insert in the liquid wires connected with the terminals of a high voltage battery or dynamo (the ordinary electric lighting circuit can conveniently be employed), one in either limb of the tube, we shall find that the sulphide of arsenic migrates towards and collects around the positive terminal. The particles of arsenic sulphide, therefore, carry a negative charge of electricity. Even with fine suspensions, such as a suspension of fine clay or a slime of peat, the same phenomenon is observed ; the clay particles

or the peat fibres collect around the positive terminal in a firm mass. Since the effect depends primarily on the voltage of the current, while only an insignificant amount of electricity is used, this process of *cataphoresis*, or electric transport of suspended particles, constitutes a very economical means of freeing a fine suspension of slime from water; and it has, in fact, found industrial application in Germany to the partial drying of very wet peat or peat slime. The high cost of fuel required to evaporate off the water from such very wet peat is thereby saved, so that it becomes possible to utilise peat-bogs which are so wet that they could not otherwise be worked with commercial success.

When a positively charged and a negatively charged colloid, such as ferric hydroxide and arsenic sulphide, are brought together, the oppositely charged particles attract one another, and this leads to a mutual flocculation and precipitation of the colloids.

The property of adsorbing and removing substances from solution which colloids possess in virtue of the large surface which they expose, together with the fact that the colloids are electrically charged, plays an important part in the processes of dyeing, in agriculture, in the purification of water and of sewage, in the life processes of animals and plants, and in many other domains.

The process of dyeing is by no means a simple one, and no single explanation can be given of the way in which dyes are, in all cases, fixed on the fibre of the material dyed. But in recent years the general advance in our knowledge of the peculiar behaviour of the

substances in the colloidal state, has led to the recognition of the important *rôle* which colloids may play in the dyeing process. Not only are the fibres of silk, wool, and cotton similar, in many respects, to colloids, more especially in possessing a structure exhibiting a largely developed surface, but many of the dye-stuffs are also colloids. In some cases the dye may be fixed on the fibre by the addition of salts, the colloidal dye being thereby precipitated in the fibre just as addition of salts produces a precipitation of colloidal sulphide of arsenic. But in other cases the process of dyeing is probably one which depends largely on a mutual precipitation of colloids having opposite electric charges, the negatively charged fibres attracting and fixing on themselves positively charged dye-stuffs.

Whilst it is found that, in very many cases, silk and wool have the power of taking up and fixing the dye-stuff directly, it is frequently found that in the case of cotton the fixation of the dye has to be assisted by a *mordant*, which is either a colloid itself or can give rise to a colloid. The colloid so formed is deposited on and within the fibre to be dyed, and attracts and fixes oppositely charged colloidal dyes. According to the nature of the dye, so must be the nature of the mordant employed, salts of aluminium, chromium, etc., which give rise to the hydroxides of the metals, being used when the dye has a negative charge or has acid properties (*e.g.* alizarin); while tannic acid and similar substances are employed for dyes with a positive charge or with basic properties. Chemical actions, however, also play an important part in the dyeing processes.

In agriculture, also, the colloidal state is of the greatest importance. In the soil there exist various colloidal substances, such as the humus, colloidal ferric hydroxide and aluminium hydroxide, clay, etc. Owing to the presence of these, soluble substances, such as the salts of potassium, phosphates, and other substances necessary for the life of the plant, are adsorbed and retained in the soil, and so kept available for the support and nourishment of vegetation instead of being washed away into the rivers and sea. The humus, moreover, being a colloid similar to albumin and gelatin, has the property of imbibing water and so helps to maintain the soil in a moist condition, while it also acts as a substrate for the bacteria concerned in the conversion of nitrogenous organic matter into such a form as can be taken up by the plants, as well as for the other bacteria always present in the soil.

Owing to the presence of such colloids as ferric hydroxide and aluminium hydroxide, filtration through soil acts as a very efficient means of purifying sewage and other waste water, from organic impurities. These impurities in sewage, for example, have been found to be, to a large extent, negatively charged colloids which are therefore precipitated and retained by the positively charged colloids, ferric hydroxide and aluminium hydroxide. By such filtration through the soil, therefore, even the highly impure water which drains from cultivated and manured land is rendered comparatively sweet and harmless. In the same way, the purification of drinking-water by filtration through beds of sand or through charcoal, depends on the removal of impurities by adsorption on the large filtering surface exposed, and on the retention of

positively charged colloidal matter, bacteria, etc., by the negatively charged sand or charcoal particles.

An important application of the behaviour just described, is found in sewage farms, where the drainage of towns is pumped on to the land and the liquid allowed to drain through the porous soil. Here, the waste organic matter is retained and affords a rich nutriment for the growing crops, while the liquid effluent which drains away is such that it might be drunk with safety. By such means can, in suitable surroundings, a source of annoyance and loss be turned to profit.

Although, in recent years, the importance of the colloidal state in its bearing on many of the activities of daily life, has become more clearly recognised and more fully appreciated, it is in connection with our conceptions of the constitution of matter that the investigations of microscopic and ultra-microscopic suspensions have gained some of their most brilliant triumphs. For more than two thousand years there has existed in men's minds the idea of matter as made up of separate, discrete particles; and in the nineteenth century, as we have seen, this idea was given a more definite form at the hands of Dalton and of Avogadro. But the particles, the molecules, which make up matter as our eyes reveal it to us, are not in a state of rest. In the case of a gas, these molecules are in a state of almost inconceivable tumult and commotion, which even the restraint imposed by the condensation and the congealing of the gas to the liquid and the solid state, is not able wholly to subdue. Such, at least, is the picture of matter which the genius of a Clerk Maxwell and a

Clausius revealed to us in what is known as the kinetic theory of matter. But although this theory has been found to give a satisfactory explanation of the behaviour, more especially of gases, and has enabled one to calculate not only the size of the molecules (roughly, one hundred millionth of an inch in diameter), but also the speed of their flight, there were not wanting some who refused to believe in the objective reality of molecules and of the picture presented by the kinetic theory. And yet, even as early as 1827, these molecules, although by their minute size removed far beyond the range of human vision, had, all unknown to their observers, made their presence manifest by their actions. In that year, the botanist Robert Brown, while examining suspensions of pollen grains under the microscope, observed that the particles were never at rest, but were in rapid motion, vibrating, rotating, moving irregularly along a zigzag path, sinking, rising,—*perpetually* in motion. In this Brownian movement, as it is called, the full significance of which has only recently been grasped—it had, indeed, been observed long ago by the French naturalist, Buffon, who saw in it a manifestation of life—we have an actual picture of that tumult and commotion of the molecules which were revealed to the mental vision of mathematical physicists. But it is not, of course, the motions of the molecules themselves that we see in the Brownian movement, but only the effect of the incessant bombardment of the coarser, visible particles of the suspension, by the molecules of the liquid.

Over a lengthened period of time, the number of blows which a suspended particle of sufficient size, say such as is visible to the naked eye, would receive from the

molecules of the liquid in which it is suspended, would be the same in the different directions. The suspended particle, therefore, would show no sign of motion. But if we imagine the period of time made sufficiently short, the number of impacts of the liquid molecules will no longer be equal in different directions, the impacts will no longer balance one another, and if the suspended particle is small enough it will, at each blow, be caused to move, first in one direction and then in another, and all the faster the smaller the particle; and it is this motion of a particle of a suspension under the blows which are rained upon it by the molecules of the liquid, that constitutes the Brownian movement. With particles of ultra-microscopic dimensions the phenomenon is exhibited with extraordinary vividness, and it is to this Brownian movement that the stability of colloidal suspensions is largely due. From the careful quantitative investigations of this phenomenon which have been carried out in recent years, the various molecular magnitudes—the kinetic energy of the particles and their velocity of diffusion, for example—have been computed; and such is the closeness of agreement between the results so obtained and the values which the kinetic theory would lead us to expect, that we cannot any longer hesitate to believe that in the rapid, darting motions of the ultra-microscopic particles we have made manifest to us something of the turbulent stir and bustle which is going on unceasingly in that under-world of molecules which lies beyond the reach of our senses.

CHAPTER XI

MOLECULAR STRUCTURE

Of all the known elements, the element carbon, familiar to us in the three physically distinct forms, charcoal, graphite, diamond, stands out pre-eminent in its power of forming compounds with other elements. So numerous, indeed, are its compounds—their number at the present day exceeding 150,000—that their study has developed into a special branch of chemistry, organic chemistry. This name is but the survival from an older period when chemists drew a distinction between the compounds occurring in the non-living, mineral world, and those occurring in the living animal and vegetable organisms, and which were thought to be producible only with the help of a special form of energy, the so-called vital force, inherent in the living cell. That any essential difference exists between the two classes of compounds, that the chemical laws which obtain within the domain of living nature are different from those which are found in inanimate nature, can no longer be held. For not only can many, very many, of the compounds which were formerly regarded as typical products of animal and vegetable metabolism, typical organic compounds in the older sense, be prepared in the laboratory from purely mineral materials, but the synthetic production of not a few of these compounds has even developed into industries of enormous

magnitude. The term, "organic chemistry," is still retained, not with its old signification, but merely as denoting the chemistry of carbon and its compounds; for, indeed, the vast majority of these "organic" compounds are found in no animal or vegetable organism, but have been prepared by the intelligent combining together of substances by the chemist.

But if I have referred particularly to the compounds of carbon, it is not for the purpose of describing either the methods of preparation or the specific properties of any of these substances, but rather for the purpose of discussing very briefly a phenomenon which, although met with in the case of the compounds of other elements, is found with extraordinary frequency in the case of the compounds of carbon. This is the phenomenon to which the name of *isomerism* has been given.

When Dalton introduced his atomic theory, the basis on which all modern chemistry has been built, he showed, as we have seen, that a compound could be regarded as being formed by the combination or uniting of the atoms of the constituent elements in certain constant and definite proportions. But whilst the law, "One compound, one composition," has remained unshaken, the progress, more especially of organic chemistry, soon showed that the converse statement, "One composition, one compound," which, to the earlier chemists, was equally an article of faith with the former, is very far removed from the truth. As the number of compounds became multiplied, it began to be more and more frequently observed, that the same elements might be united in the same proportions and yet yield compounds with entirely different properties. More than a hundred different

compounds, for example, can be produced by the combining together of nine atoms of carbon, ten atoms of hydrogen, and three atoms of oxygen. To this phenomenon, that different compounds may have the same composition, the term *isomerism* has been applied. Just as the same set of bricks can, by varying their arrangement, be formed into structures of totally different kinds, so also the same atoms can, by varying their arrangement within the molecule, give rise to different atomic structures, or different compounds. In other words, the discovery of isomerism, so entirely unforeseen by Dalton and by the earlier organic chemists, led to the recognition of the fact that the properties of a compound depend not merely on its composition, but also on its internal structure or the arrangement of the atoms within the molecule; and our knowledge of a substance is not complete until we know what is this internal structure or *constitution* of the molecule.

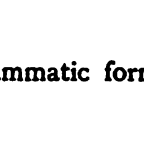
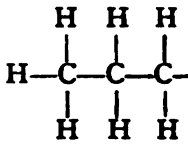
A knowledge of the constitution is essential for the successful building up or synthesis of a compound from simpler materials, which we shall discuss more fully in the following chapter. To elucidate the constitution of the different compounds, is one of the main aims of the organic chemist, and in the case of the more complex compounds, the problem becomes one of the greatest difficulty. Only this much can be said here. Through the laborious efforts of numberless chemists, a knowledge has been gradually accumulated of the internal structure or constitution of a very large number of substances, and also of the relations between these different structures and the physical and chemical properties of the compound. In order to determine the constitution of an unknown compound, therefore,

the substance is, by various chemical actions, broken down into bits, as it were, and one then seeks to identify the fragments, the simpler substances, so obtained, with substances of which the constitution is already known. From the knowledge gained in this way, one then attempts to piece the fragments together again, and so to build up or synthesise the original substance.

But the task of elucidating the constitution of organic compounds would be a hopeless one without the aid of some guiding principle and some method by which the molecular constitution can be represented. It was, therefore, a great step in advance when Kekulé, in 1858, showed how molecular constitutions could be represented diagrammatically, using as a guiding principle what is known as the doctrine of *valency*.

This doctrine of valency, the introduction of which we owe mainly to the late Sir Edward Frankland, is merely a recognition of the fact that the elementary atoms do not possess an unlimited power of combination. Hydrogen and chlorine, for example, can combine together only atom for atom; an atom of hydrogen cannot combine with more than one atom of chlorine, and an atom of chlorine cannot combine with more than one atom of hydrogen. No element is known having a lower combining power than hydrogen, and this is therefore taken as the standard of reference. Chlorine, an atom of which can combine with only one atom of hydrogen[1] is said to have unit combining power, or unit valency; it is univalent. Oxygen, an atom of which can combine with two atoms of hydrogen (as in water, H_2O), is said to be bivalent; nitrogen, an atom of which can combine with three atoms of hydrogen,

is said to be tervalent; carbon, an atom of which can combine with four atoms of hydrogen, is said to be quadrivalent; and so on.

Although there is, of course, no material link or bond between the atoms, we can nevertheless represent union between atoms as if it were material, by means of a line, or lines, according to the valency of the atom. Thus, as we have already seen, we can represent the compound marsh-gas by the diagrammatic formula  , and the higher hydrocarbons of that series by such a chain of carbon and hydrogen atoms as  ; a formula which we can also write in the simpler form, $CH_3—CH_2—CH_3$. By the extension of this idea, it became possible not only to represent the molecular constitution of known compounds, but also to foresee the possible existence of isomeric compounds. Thus, for example, if we have the compound $CH_3.CH_2.CH_3$, (the bond between the carbon atoms being now represented by a dot), it is clear that we can replace one atom of hydrogen in this compound by an atom, say, of chlorine, in two ways, so that we should obtain either the compound $CH_3.CH_2.CH_2Cl$, or the compound $CH_3.CHCl.CH_3$, the chlorine being in the former case attached to a terminal carbon atom and in the latter case to the intermediate carbon atom. According to this, there should exist two and only two

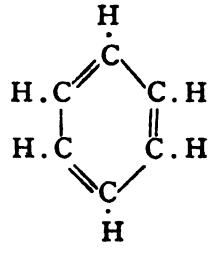
different compounds having the composition C_3H_7Cl; and as a matter of fact two compounds and only two are known.

The origin of this theory of chemical structure has been recounted by Kekulé himself. During a period of residence in London he was returning from a visit paid at Islington to where he stayed at Clapham. "One fine summer evening," he relates,[1] "I was returning by the last omnibus, 'outside' as usual, through the deserted streets of the metropolis, which are at other times so full of life. I fell into a reverie, and lo! the atoms were gambolling before my eyes! Whenever, hitherto, these diminutive beings had appeared to me, they had always been in motion; but up to that time, I had never been able to discern the nature of their motion. Now, however, I saw how, frequently, two smaller atoms united to form a pair; how a larger one embraced two smaller ones; how still larger ones kept hold of three or even four of the smaller; whilst the whole kept whirling in a giddy dance. I saw how the larger ones formed a chain," . . . And then he adds: "I spent part of the night in putting on paper at least sketches of these dream-forms." From these sketches were developed the constitutional or structural formulæ, of which examples have just been given.

But again he had a dream. Now he was at Ghent, and dozed before his fire. Again he saw the atoms gambolling before his eyes, the chains twining and twisting in snake-like motion. "But look! What was that? One of the snakes had seized hold of its own tail, and the

[1] F. R. Japp, "Kekulé Memorial Lecture" (*Transactions of the Chemical Society*, 1898).

form whirled mockingly before my eyes. As if by a flash of lightning I awoke;" . . . but the picture Kekulé had seen of the snake which had seized its own tail gave him the clue to one of the most puzzling molecular structures, the structure of the benzene molecule, a ring of six carbon atoms to each of which a hydrogen atom is attached. Thus we obtain the structural formula of the benzene molecule,



the "ring" of carbon atoms being written in the form of a hexagon instead of in the form of a circle. "Let us learn to dream," said Kekulé, "then perhaps we shall find the truth." But he wisely added: "But let us beware of publishing our dreams before they have been put to the proof by the waking understanding."

By the introduction of the doctrine of valency and of Kekulé's diagrammatic method of representing molecular constitution, a satisfactory basis seemed to have been obtained for the future development of organic chemistry. And yet, it was not long before the insufficiency of this theory of chemical structure became only too apparent, owing to the discovery that, in some cases, the number of isomeric compounds is greater than can be represented by the structural formulæ of Kekulé. A new isomerism

was discovered, an isomerism which manifested itself in the property known as *optical activity*.

Early last century it was discovered that when a ray of light is passed through a crystal of Iceland spar, the ethereal vibrations, which propagate the light, and which, ordinarily, take place in all directions at right angles to the path of the ray, are all brought into one plane. The light is said to be *polarised*. When, now, this polarised light is passed through certain substances, quartz, turpentine, a solution of cane sugar, etc., it is found that the plane of polarisation, the plane in which the ethereal vibrations take place, is rotated or twisted, this rotation or twisting taking place sometimes to the right, sometimes to the left; an effect which we can illustrate by the twisting of a strip of stout paper into a right-handed or left-handed spiral, such as is represented in Fig. 17. Substances which possess this property of rotating the plane of polarised light, are said to be "optically active."

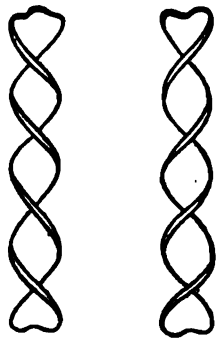


FIG. 17.

This property of optical activity can also be demonstrated by a modification of a very interesting experiment due to the late Sir George Stokes. When a beam of light from a projection lantern (Fig. 18), is reflected vertically downwards by means of a mirror, through a column of water rendered slightly turbid by the addition of a few drops of an alcoholic solution of rosin, the path of the beam is rendered visible by the fine suspension of rosin particles (Tyndall phenomenon, p. 189); and the

beam of light appears equally bright all round. But if the light from the lantern is first polarised by passage through a prism of Iceland spar, and then reflected downwards through the column of water, the appearance obtained is that of a band which is light *only on two* opposed sides, and dark on the other two opposed sides. On rotating the prism of Iceland spar, the band also rotates and turns alternately its light and dark sides to the eye. The effect

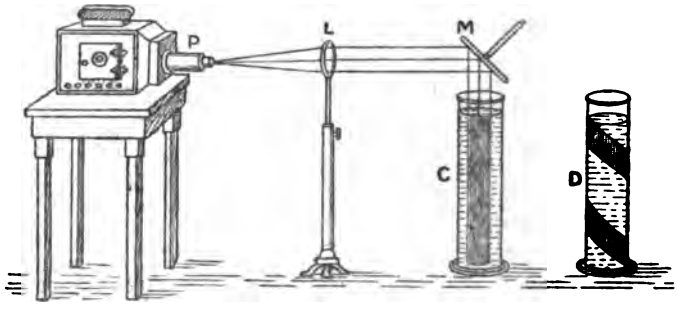


FIG. 18.—DEMONSTRATION OF THE POLARISATION OF LIGHT.

Light from a lantern is polarised by passage through the polarising prism P, and the beam of light is then directed by the lens L on to a mirror M, by which the light is directed vertically downwards through water contained in the cylinder C, and rendered turbid by a fine suspension of rosin. A vertical, polarised band of light is obtained. If the cylinder C is replaced by D, which contains a concentrated solution of cane sugar, the band of light is twisted into the form of a spiral.

produced is as if the beam of light on passing through the prism of Iceland spar, were given a flat form, like a book, from the two opposite edges of which light is emitted, while the sides remain dark. Thus we have illustrated the phenomenon of polarisation of light. If, now, the cylinder of water is replaced by a cylinder containing a solution of cane sugar, the band of light is twisted into a spiral form, and on rotating the prism of Iceland-spar, this spiral band of light will appear to move with a

LOUIS PASTEUR, 1822-1895.
(*From a Photograph by Pierre Petit.*)

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screw-like motion. From the fact that the different rays of coloured light which together constitute white light, are twisted or rotated to different extents (the blue rays being rotated more than the red), the spiral band of light shows the colours of the rainbow.

What then is the explanation to be given of this remarkable property of substances, the study of which, starting with the brilliant discoveries of Pasteur in 1848, has occupied the attention of many of our foremost chemists down to the present day?

When Pasteur commenced the investigations which were to initiate a revolution in the current ideas regarding the molecular structure of organic compounds, two isomeric acids were known having the same composition, namely, tartaric acid and paratartaric acid. The former, which is found occurring in grape juice, is optically active; the latter is inactive. On examining the crystals of these two acids, and of a number of their salts, Pasteur found that whereas the crystalline faces of the inactive paratartaric acid and its salts, were all fully developed, and the crystals symmetrical (Fig. 19); in the case of the active tartaric acid, the full development of the crystalline faces was interrupted by the occurrence of so-called hemihedral faces (Fig. 20). The occurrence of these hemihedral faces was regarded by Pasteur as the outward and visible manifestation of the property of optical activity, in accordance with a view which had been suggested by Sir John Herschell in the case of crystalline quartz, which is also optically active. But whereas quartz is optically active only in the crystalline state, tartaric acid retains the property even when dissolved. In the former case, the property depends on the

crystalline structure, in the latter, it depends on the internal molecular structure.

But a further discovery was made by Pasteur. During his investigation of one of the salts of tartaric and paratartaric acid (namely, sodium ammonium tartrate and sodium ammonium paratartrate), Pasteur found, as was to be expected, that the crystals of the tartrate resembled those of the other tartrates he had examined in possessing hemihedral faces, arranged in a similar manner. The crystals obtained from the solution of the

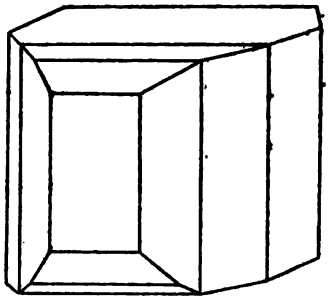

FIG. 19.—HOLOHEDRAL CRYSTAL OF PARATARTARIC ACID.

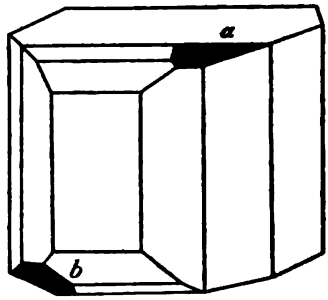

FIG. 20.—CRYSTAL SHOWING HEMIHEDRAL FACES.

paratartrate, however, instead of being holohedral, with the crystalline faces fully developed, were found also to have hemihedral faces; but these hemihedral faces, instead of, as in the tartrates, all being turned the same way, were inclined, sometimes to the right and sometimes to the left (Fig. 21). This result was quite unexpected; and Pasteur, on carefully separating the two sets of crystals and examining their solutions, discovered, with no less surprise than pleasure, that one set of crystals rotated the plane of polarised light to the right, while the other set rotated the plane by an equal amount to

the left. On dissolving together equal amounts of the two sets of crystals, a solution was obtained which was quite inactive.

Here, then, we have the discovery of that new kind of isomerism to which reference has just been made, and which showed the insufficiency of the structural formulæ of Kekulé. The two salts into which the paratartrate had been separated were identical in all their chemical and physical properties, save only in the disposition, to the right or to the left, of the small hemihedral faces occur-

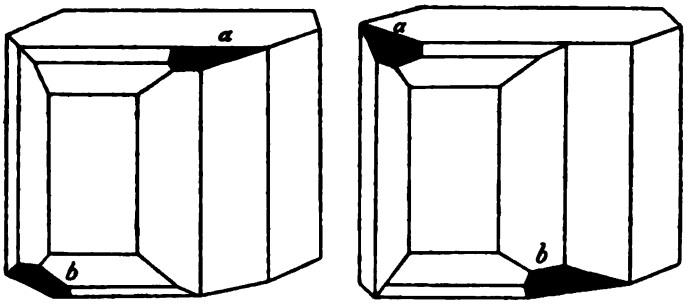

FIG. 21.—ENANTIOMORPHIC CRYSTALS OF OPTICALLY ACTIVE TARTRATES.

ring on their crystals, and in the property of rotating the plane of polarised light to an equal extent but in opposite directions. From these two salts, Pasteur obtained two different tartaric acids; one having the power of rotating the plane of polarised light to the right and identical with the acid occurring in grape juice, the other, hitherto unknown, and having the power of rotating the plane of polarised light to the left. Moreover, on mixing together in solution equal quantities of these two optically active acids, there separate from the solution crystals of the

inactive paratartaric acid, which is thus shown to be a compound of the two active acids in equal proportion.

The discovery of the two optically active tartaric acids was a momentous one, effecting a revolution in the views of chemists regarding molecular structure; and we can well understand the feeling of happiness and the nervous excitement by which Pasteur was overcome on making the discovery. Rushing from his laboratory and meeting a curator, he embraced him, exclaiming: "I have just made a great discovery! I have separated the sodium ammonium paratartrate into two salts of opposite action on the plane of polarisation of light. The dextro-salt is in all respects identical with the dextro-tartrate. I am so happy and overcome by such nervous excitement that I am unable to place my eye again to the polarisation apparatus." But the question now arose as to how the existence of the two optically active tartaric acids could be accounted for.

All material things belong to one or other of two classes, according as the image which is formed of the object in a mirror, is such that it could or could not be superposed on the object. In the case of a cube, for example, the image formed in a mirror is identical with the object, and we can imagine the image superposed on the original cube. A cube is a symmetrical object. But if a right hand is held in front of a mirror, the image which is obtained represents a left hand, and this cannot be superposed on the right hand; a right hand will not fit into a left-hand glove. In the case of a hand, therefore, we have an asymmetrical object, which can exist in two distinct, so-called *enantiomorphic* forms, similar in all

respects, but not superposable, not identical. And when we examine the crystals of the two optically active tartaric acids (or of their salts), it is seen that they also are related to each other as the right hand is to the left hand; each represents the non-superposable mirror image of the other (Fig. 21), and the two crystals, although in all points similar, are not identical. If, however, the crystalline form is to be regarded, as Pasteur regarded it, as a visible manifestation of the internal structure, we are led to the conclusion that the *molecular* structures of the two active tartaric acids are asymmetric and enantiomorphously related to each other as object to non-superposable mirror image. "Are the atoms," Pasteur asked, "are the atoms of the dextro-acid grouped in the form of a right-handed helix, or do they stand at the corners of an irregular tetrahedron, or are they arranged in some other asymmetrical manner?" And he replied, "We are not yet in a position to answer these questions. But it cannot be a subject of doubt that there exists an arrangement of the atoms in an asymmetric order, having a non-superposable image."

Looking back on the experimental investigations of Pasteur, we cannot suppress a feeling of disappointment that it was not vouchsafed to him, with the clear views he possessed regarding chemical structure, to take but a little step forward and to develop these views into a theory of chemical structure. But the time was not yet ripe, and it was not until after more than twenty years that the study of organic chemistry furnished a sufficient number of examples of optically active compounds, to make it possible to give an answer to Pasteur's questions.

Nevertheless, Pasteur introduced into chemistry a conception of extraordinary importance and fruitfulness, the conception of *molecular asymmetry*, and he recognised that molecular structure is not a matter of two dimensions only, but of three. The atoms are not arranged in a plane, as the formulæ of Kekulé represent them, but in three-dimensional space. In this way Pasteur inaugurated a new chemistry, a "Chemistry in Space" or "Stereo-Chemistry."

The conception of molecular asymmetry and the idea of the grouping of the atoms at the corners of an irregular tetrahedron were developed, in 1874, into a

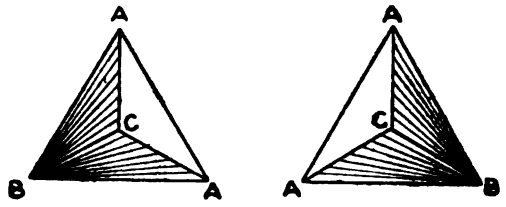

FIG. 22.

consistent theory of molecular structure, embracing the optically active isomeric compounds, by a Dutch and a French chemist independently, van't Hoff and Le Bel.

If we imagine a carbon atom at the centre of a tetrahedron, and if the four atoms or groups, with which, as we have seen, a carbon atom can be united, are situated at the four corners of the tetrahedron, it will be found that so long as two, at least, of the atoms or groups are the same, the molecule, represented as a tetrahedron, will be symmetrical and its mirror image will be superposable on and therefore identical with the original. This will be clear from an inspection of Fig. 22,

which represents such a tetrahedron and its mirror image. The right-hand tetrahedron, obviously, only requires to be turned through an angle of 90°, on the corner B as a pivot, to become identical in disposition with the left-hand tetrahedron.

If, however, the four atoms or groups attached to the carbon atom are all different, the molecule, as represented by the tetrahedron, becomes asymmetric, and gives a mirror image which is no longer superposable on the original. Two isomeric forms are therefore possible. This will be understood from Fig. 23. Viewing these tetrahedra

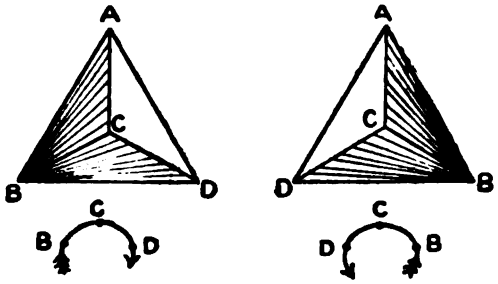

FIG. 23.

from a similar position, we see that the groups B C D, in the one case, are arranged from left to right; in the other case, from right to left. If one of these represents a molecule which rotates the plane of polarised light to the right, the other will represent a molecule which rotates the plane of polarised light to the left.

The views of van't Hoff and Le Bel have received the amplest confirmation. Not only has it been found that all compounds which are optically active do contain at least one atom of carbon to which four different atoms or groups are attached—a so-called *asymmetric carbon*

atom—but also, no compound has been obtained the possible existence of which could not be predicted by means of the van't Hoff and Le Bel theory. So fruitful has the conception of molecular asymmetry and of the asymmetric carbon atom proved, that it has been extended also to the atoms of other elements than carbon, of which optically active isomers have been prepared.

We have already seen that in the case of tartaric acid —and the same holds in all other cases of optically active substances—there exist, or can exist, not only the two optically active isomers, but also an inactive isomer, produced by the combination of the two oppositely active forms in equal amounts, and separable again, by suitable means, into the active forms. This inactive form is known as the *racemic* form. In the case of one particular salt, sodium ammonium paratartrate, as we have seen, this breaking up of the racemic form (the paratartrate) takes place on crystallising from water at the ordinary temperature. But this method is capable of only a limited application. Pasteur, however, introduced two other methods for effecting the resolution of the racemic into the active forms or for obtaining one of the active forms separate from the other, namely, by making use of some living organism or of some other asymmetric, optically active material. When, for example, the solution of the racemic paratartaric acid is acted on by blue mould, *Penicillium glaucum*, the fungus feeds on and destroys the dextrorotatory acid, which occurs naturally in grapes, but leaves unchanged the lævo-acid, which is an artificial product of the laboratory. The solution, therefore, becomes

lævorotatory, and the lævo-acid can be obtained by concentrating the solution and allowing it to crystallise. In the process of fermentation, also, under the action of various enzymes, which are themselves asymmetric agents, produced in the living animal and vegetable cells, we find a similar selective action. Thus, whereas the dextro-rotating glucose, the well-known grape sugar, undergoes fermentation, the lævo-rotating glucose, a compound only obtained artificially, remains unchanged in the presence of yeast. An asymmetric agent acts only on materials of similar asymmetry to itself, just as a right-handed screw will only fit into a right-handed thread. *So long as the two optically active isomers are brought into relations with symmetrical agents, they behave identically; but when they react with an asymmetric agent, a different behaviour is exhibited by the two forms.*

This selective action is of great physiological importance, since in all the life processes, such as digestion and assimilation, we are dealing with the action of the optically active, asymmetric materials contained in the cells and tissues. We find, therefore, that although the naturally occurring albumins and sugars, for example, are capable of being digested, the isomeric compounds of opposite activity pass through the body without being absorbed. And a similar differentiation of action is met with in the case of many of the optically active alkaloids. "Here, then," said Pasteur, "the molecular asymmetry proper to organic substances intervenes in a phenomenon of a physiological kind, and it intervenes in the *rôle* of a modifier of chemical affinity. . . . Thus we find introduced into physiological principles the idea of the influence of the

molecular asymmetry of natural organic products, of this great character which establishes, perhaps, the only well-marked line of demarcation that can at present be drawn between the chemistry of dead matter and the chemistry of living matter."

In the investigation of molecular structure, the study of optically active substances has been of supreme importance, and the knowledge which has been gained has exercised an important influence on the understanding and interpretation of biological processes, opening to physiology, as Pasteur said, new horizons, distant but sure. But it is not merely the domain of the material sciences which has been enriched by the investigations of stereo-chemistry; the most fundamental problems of life, our very ideas with regard to life itself, and the phenomena of life, receive illumination.

Until 1828, as we have seen, the production of the organic substances occurring in the animal and vegetable organisms was considered to be the prerogative of life; but the synthetic production in the laboratory of many of the compounds which are typical products of the animal and vegetable organism, led to the abandonment of that belief, and science began to look upon the phenomena of life as completely explicable in terms of physics and of chemistry. But the discovery and investigation of the optically active compounds introduced a new factor. As Professor F. R. Japp, in his Presidential Address to the Chemical Section of the British Association in 1898, so admirably emphasised, "the phenomena of stereo-chemistry support the doctrine of vitalism as revived by the younger physiologists, and point to the existence of a directive force

which enters upon the scene with life itself, and which, whilst in no way violating the laws of the kinetics of atoms, determines the course of their operation within the living organism."

In Nature, most asymmetric compounds are found occurring in *one* of the optically active forms only. Dextro-rotatory tartaric acid, for example, occurs in grape juice, but the lævo-rotatory tartaric acid is not found in Nature, and is known only as a laboratory product; grape sugar likewise occurs naturally only as the dextro-rotatory form; while the albumins are lævo-rotatory. When, however, it is attempted to prepare an asymmetric compound in the laboratory from symmetric substances only, from substances, that is to say, which are not themselves optically active, it is always found that the product obtained is *inactive*. As Pasteur said: "Artificial products have no molecular asymmetry; and I could not point out the existence of any more profound distinction between the products formed under the influence of life and all others."

It is true that the inactive, racemic form, which is obtained as the result of the artificial synthesis, can be separated into the two optically active forms, with the help of asymmetric, optically active compounds; or we can even, by the process of fermentation or the action of organisms, destroy one of the active forms and so obtain a single optically active compound. But these processes involve the use either of living organisms or of materials which have been produced by living organisms, and the production of the active form is, therefore, due directly or indirectly to living matter. But, as we have seen, Pasteur also found that, in some cases, the resolution of the racemic

form can be effected simply by crystallisation. By allowing a solution of the inactive racemic sodium ammonium paratartrate to crystallise, crystals of the dextro- and of the lævo-rotatory sodium ammonium tartrate were, as we have already seen, deposited separately, and could, owing to the difference in their crystalline forms, be distinguished from one another and be separated by hand. Since the original racemic paratartrate could be prepared synthetically from symmetrical materials by the action of only symmetrically acting reagents, and since this racemic form could be resolved into the active forms by the symmetrically acting process of crystallisation, it was thought that "the barrier which M. Pasteur had placed between natural and artificial products" had been thereby broken down. And this was undoubtedly the view held by the majority of chemists.

But was this view—a view still held by many—correct? Pasteur certainly did not think so, and he pointed out very pertinently, that "to transform one inactive compound into another inactive compound which has the power of resolving itself simultaneously into a right-handed compound and its opposite, is in no way comparable with the possibility of transforming an inactive compound into a *single active* compound. This is what no one has ever done; it is, on the other hand, what living nature is doing unceasingly before our eyes." The artificial, racemic compound certainly, had been resolved into the two active forms by the symmetrical process of crystallisation, but these two forms had not been *separated* from each other; both active forms were present side by side. Their separation "requires the living operator, whose intellect embraces the conception of opposite forms of symmetry." But, as

Professor Crum Brown asked long ago: "Is not the observation and deliberate choice by which a human being picks out the two kinds of crystals and places each in a vessel by itself, the specific act of a living organism of a kind not altogether dissimilar to the selection made by *Penicillium glaucum?*", a mould which, as we saw, destroys one optically active form but not the other.

While Pasteur certainly believed that all the attempts which had been made to synthesise a single optically active form, without the intervention, direct or indirect, of life, had been unsuccessful, he appears to have held the view that as science advanced, the inability to effect such a synthesis might be removed, for while he recognised the necessity for the existence of asymmetric forces "at the moment of the elaboration of natural organic products," he conceived the possibility that such asymmetric forces might lie outside the living organism and "reside in light, in electricity, in magnetism, or in heat." This view, certainly, is one that cannot be dismissed off-hand, and some see in circularly polarised light an asymmetric agent which might account for the production in nature of single optically active forms. But the suggestions and experimental evidence which have been offered in support of this view cannot certainly be regarded as convincing. Whatever of fuller knowledge and more successful achievement the future may hold, one thing, at least, may be said now—that all attempts to synthesise a single optically active compound under the influence of circularly polarised light or of magnetic or other purely physical forces, have met with failure. And if the evidence of stereo-chemistry is to be accepted, it points to the conclusion, to quote the words

of Professor Japp, that "at the moment when life first arose, a directive force came into play—a force of precisely the same character as that which enables the intelligent operator, by the exercise of his will, to select one crystallised enantiomorph and reject its asymmetric opposite."

CHAPTER XII

SYNTHETIC CHEMISTRY

IT may, perhaps, have seemed to some that however interesting, as an intellectual speculation, the theories of molecular structure discussed in the previous chapter might be; however much they might satisfy a philosophical curiosity regarding the mystery which lies at the heart of things, they could be of very little practical importance and could scarcely come at all into direct touch with the daily life of mankind. And yet, these theories form the very basis and foundation of some of the greatest industries of the present day! Kekulé's dreams, perhaps, were an interesting psychological phenomenon, but the stuff that his dreams were made of, the theories of molecular structure, were as important for the advance and development of organic chemistry, as a chart and compass are for a mariner. For, the purpose of a scientific theory is not merely to explain or co-ordinate knowledge already acquired, but also to be a guide to the exploration of the unknown; and without the theories of molecular structure or constitution put forward by Kekulé, van't Hoff and Le Bel, there could not have been built up that vast structure of organic chemistry such as we know it at the present day, nor could we have witnessed

that crowning achievement of organic chemistry, the artificial, synthetic preparation of many of Nature's own products, from which has developed the industrial production of those innumerable dyes, therapeutic agents, perfumes, and other materials, which are regarded as necessaries in our modern civilisation.

But while the theories of molecular structure and constitution gave the guidance necessary for the altogether phenomenal development of organic chemistry during the past sixty years, that development could actually take place only through the genius, the energy and the persistence of hundreds of zealous workers who devoted themselves to the task of synthesising and elucidating the constitution of thousands of organic compounds, and it is therefore only natural that it is in that country—Germany—which amongst all other countries has been conspicuous for its recognition of the importance of such investigations, and for the encouragement which it has given to them, that we find the industries dependent on synthetic organic chemistry chiefly flourishing.

Not only has the chemist discovered numberless compounds hitherto unknown, but he has even entered into competition with Nature herself, and has successfully broken the monopoly which heretofore she had enjoyed in the production of many compounds both of ornament and of utility. In fact, so successful has the chemist been, that not only can the artificial products, in a number of cases, compete with the natural products, but they have even driven these entirely out of the market. In this way great industries have arisen, of which the most important are those closely interdependent industries which find their

raw materials mainly in coal tar, and it is to these that we shall first turn our attention.

By the distillation of coal there is obtained not only the gaseous mixture so largely employed as an illuminant, but also considerable amounts of ammonia and a thick, dark-coloured, evil-smelling liquid, coal tar—one of the most valuable and important materials obtained by man. It is not an attractive-looking material, and yet there have been evolved from it, by the painstaking labours of a multitude of chemists, substances innumerable—dyes by the thousand, which rival in range and beauty of tone the finest products of Nature's imagining; explosives which the strongest works of man are powerless to resist; antiseptics and drugs; the sweet-smelling essences of flowers; and developers of the latent photographic image. This coal tar is, indeed, an almost inexhaustible storehouse of raw materials for the manufacture of products of manifold variety.

By subjecting the crude coal tar to a process of distillation, such as is done in the refining of crude petroleum, various substances are obtained which distil over at different temperatures. Of these the most important are the following:—

LIQUIDS.

	b.p.
Benzene	176° F.
Toluene	230° F.

SOLIDS.

	m.p.
Phenol (carbolic acid)	106° F.
Naphthalene	174° F.
Anthracene	415° F.

Benzene, or as it is frequently called in commerce, benzol, forms the starting-point in the manufacture of aniline (which can be regarded as benzene in which one of the atoms of hydrogen is replaced by the group NH_2); and this, in turn, is the starting-point in the preparation of a large number of dyes—the aniline dyes. These aniline dyes, which were the first synthetic dyes to be prepared, constitute, however, only a part of the total number of dyestuffs which are now manufactured from coal-tar products.

Toluene (commercially, toluol) is used as a raw material in the manufacture not only of dyes, but also of the powerful high explosive, trinitrotoluene, or T.N.T.

Phenol or *Carbolic Acid*, is a well-known antiseptic, and is also the starting-point in the preparation of the explosive picric acid, lyddite or melinite. It is also used in the manufacture of dyes.

Naphthalene is a valuable constituent of coal tar. It is the raw material chiefly employed in the manufacture of indigo.

Anthracene is the raw material employed in the manufacture of a large number of important dyes, the most familiar of which is the red dye, alizarin, or Turkey red.

Important as these different substances are, they constitute only a small part of coal tar, the amounts in which they occur being, moreover, dependent not only on the nature of the coal used but also on the temperature at which the coal is distilled. Thus, the benzene and toluene together constitute about 3 per cent., phenol about 1 per cent., naphthalene about 5 per cent., and anthracene about 0·5 per cent. of the coal tar formed in gas manufacture. By the distillation of one ton of coal, therefore,

we should obtain the above constituents in the following quantities, roughly:—

Benzene and Toluene	3½ lbs.
Phenol	1¾ lbs.
Naphthalene.	6 lbs.
Anthracene	10 ozs.

The Coal-Tar Dyes.

Until the middle of last century, men were dependent for all the dyes with which they coloured their bodies or their garments, on colouring matters which were chiefly of animal and vegetable origin: the colouring matter of logwood; the animal dye, cochineal; the blue dye, indigo or woad, with which our ancestors in these islands are said to have stained their bodies; the red dye, alizarin, obtained from the root of the madder plant, once extensively cultivated in Southern Europe; and the costliest of all dyes, the most famous dye of the ancient world, the Tyrian purple, obtained from a shell-fish (*Murex brandaris*) found on the eastern shores of the Mediterranean.

"Who has not heard how Tyrian shells
Enclosed the blue, that dye of dyes
Whereof one drop worked miracles,
And coloured like Astarte's eyes
Raw silk the merchant sells?"

(Browning: *Popularity.*)

These dyes, and a few others, were all that were available until the year 1856. In that year the first synthetic dye, the once favourite mauve, was prepared by the late Sir W. H. Perkin, by the oxidation of crude aniline, and since that time colouring matters to the number of several thousands have been discovered by the chemist. The natural dyes are mostly of a pronounced, even crude

colour, but the products of the chemist are of an almost infinite variety; and, far out-rivalling the natural dyes in range of colour and delicacy of tone, they have ousted these dyes from the dye-works. Starting from benzene, naphthalene, and anthracene, constituents of the dirty-looking liquid, coal tar, which less than a hundred years ago was a useless waste material and a nuisance to the gas manufacturer, synthetic dyes to the value of over £20,000,000, are manufactured annually, more than three-quarters of this amount being produced in Germany.

It is quite impossible here to enter into a discussion of the composition and constitution of the coal-tar dyes, some of which are among the most complex of the compounds of carbon; but it may be said that the technique of dye manufacture has become so perfected, and our knowledge of the variation of colour with the constitution of the compound has become so well established, that the synthetic production of new shades is no longer a haphazard process, but one of which the conditions of success are clearly known.

But it is, perhaps, in the artificial production of Nature's own colouring matters, more especially of alizarin and indigo, that organic chemistry has achieved its most striking successes. Through the labours of many chemists the composition of these natural products was determined and their constitution or molecular structure unravelled, and with the knowledge thus obtained chemists have succeeded in preparing these compounds artificially—not merely substitutes for or imitations of the natural products, but the actual products themselves—and that more cheaply than Nature herself can produce them.

Forty or fifty years ago, over the whole of Southern Europe, and eastwards to Asia Minor, great tracts of land were devoted to the growing of the madder plant; in France alone, 50,000 acres were devoted to its culture. When the roots of this plant were allowed to ferment, a substance alizarin, so called from the name given by the Arabs to the madder root, was formed, which was capable of dyeing cotton of a bright red colour—the so-called Turkey red, one of the oldest of dyes and most largely used in the dyeing of cotton goods. But these madder fields have now all disappeared; for when the composition and nature of this dye-stuff had once been ascertained, it was not long before chemists discovered a method by which the dye could be manufactured from what was then practically a waste material, anthracene, one of the constituents of coal tar. By a series of comparatively simple reactions one could pass from the hydrocarbon anthracene ($C_{14}H_{10}$) to anthraquinone ($C_{14}H_8O_2$), and from anthraquinone to dihydroxy-anthraquinone or alizarin [$C_{14}H_6O_2(OH)_2$]. In this way the madder dye can be manufactured much more cheaply than Nature can produce it, and instead of the 750 tons of alizarin extracted from madder roots in 1870, over 2000 tons are now manufactured annually in chemical works.

The fate of the madder threatens also to be the fate of another dye-producing plant (*isatis tinctoria*) from which the much prized dye-stuff, indigo, has for thousands of years been obtained. Even as late as the seventeenth century, the woad was cultivated in Europe, but with the opening up of trade with the East, the European dye could not hold its own with the cheaper indigo obtained from the

Indian plantations; and these, until recently, controlled the markets of the world. But even they have not been able to stand against the march of science, and, in the production of synthetic indigo, the conquest of Nature by the chemist and manufacturer constitutes one of the most striking features of the nineteenth century. The fight was a long one, and I know of no other case in which the genius and resourcefulness of the chemist and the persistence and enterprise of the directors of German chemical industry, *themselves expert chemists*, have been so conspicuously shown, as in the successful industrial production of this dye. Let me try to recount, in the briefest possible outline, the achievement which has already become historic.

As far back as 1880, the artificial production of indigo was first achieved by the German chemist, Adolf von Baeyer, using as raw material the substance toluene, which, as we have seen, is one of the constituents of coal tar. But although this laboratory production of indigo constituted an achievement of the highest scientific importance, the chemical manufacturer strove in vain to use this discovery in his struggle to oust the natural product. Indigo certainly could be manufactured, and manufactured in quantity, but—and this is the whole essence of the matter—the artificial indigo cost more than the natural, and the raw material, toluene, was not procurable in sufficient amount to make the displacement of the natural indigo possible. For seventeen years the struggle went on, the chemist assisting with his brains and experience, the manufacturer assisting with his money, until at last, in October, 1897, after many attempts and many failures,

and the expenditure of close on £1,000,000, synthetic indigo (indigo, that is, prepared by the skill of man from simpler substances), was placed on the market in competition with the natural product from the Indian plantations. And what, to-day, is the result of this competition? Hear how eloquently the following figures speak. In 1896 India exported indigo to the annual value of over £3,500,000; in 1913 her exports of this dye were worth about £60,000, while the German export was valued at about £2,000,000. Moreover, in the above period, the price of indigo fell from about 8*s.* to about 3*s.* 6*d.* per lb.

Since the production of indigo involves a considerable number of different processes, and requires the use of a number of different substances, of which sulphuric acid, ammonia, chlorine, and acetic acid are the chief, the success of the synthesis as a whole, depends on the success with which each step of the process can be carried out, and on the cost of the substances employed. The starting-point in the manufacture is the hydrocarbon naphthalene, a constituent of the invaluable coal tar, and familiar to all on account of its use in preserving furs against the attack of moths; and the first step in the synthesis of indigo is to convert this naphthalene into a compound called phthalic acid. This, it was known, could be done by heating the naphthalene with strong sulphuric acid; but when the manufacturer attempted to make use of this fact, he found that although the desired conversion did indeed take place, it did not proceed sufficiently readily, and the cost of carrying out this first step in the process was so great that it would have rendered the industrial production of indigo unremunerative. But here a lucky

accident came to the assistance of the manufacturer, for, through the accidental breaking of a thermometer, it was discovered that mercury acts as an efficient catalyst in the conversion of naphthalene to phthalic acid, facilitating the process to such a degree as to allow it to be carried out with commercial success.

But the commercial success of the production of indigo depended also on improvements being effected in the manufacture of the various chemicals employed. Thus the demand for a very concentrated sulphuric acid and the fact that during the process of heating with naphthalene, large quantities of sulphur dioxide are formed, led to the development of a new method of making the acid, namely, by the "contact process" to which we referred in Chapter VI. For the production of chlorine, also, of which enormous quantities are required, the old method of obtaining the gas from hydrochloric acid was useless, and a new method had to be introduced, namely, by passing a current of electricity through a solution of common salt, the chlorine being then obtained in a pure state by liquefaction. The ammonia is obtained, as we have seen, as a product of the distillation of coal and can now also be prepared synthetically; and the acetic acid, of which 3000 tons are used annually in the manufacture of indigo, is obtained by the distillation of 150,000 cubic yards of wood.

The industrial production of synthetic indigo, albeit benefiting mankind as a whole, has not only dealt a mortal blow at the prosperity of the Indian plantations, but it has revolutionised two other industries, the manufacture of sulphuric acid, a staple chemical industry of

England, and of chlorine, together with that of the bleaching material prepared from it, bleaching powder.

Although it is not possible to enter into a detailed discussion of the practical process of dyeing, it is of interest to note that the process is different in the case of indigo and other so-called vat dyes, from what it is in the case of other dye-stuffs. On account of its insolubility, the indigo is first converted into a colourless compound, called indigo-white, which is soluble in alkalies. After the material to be dyed, which may be cotton, wool, or silk, has been immersed in this solution, it is removed and exposed to the air, whereby the oxygen of the air oxidises the colourless indigo-white to indigo-blue. The dye is, therefore, developed in the fibre after its removal from the bath.

Closely related, chemically, with indigo, is that other ancient dye, Tyrian purple. Some years ago the nature of this dye was investigated by a German chemist who extracted it from the glands of two species of marine snail, the *Murex brandaris* and *Murex trunculus*, and ascertained that this "dye of dyes, whereof one drop worked miracles," was a compound of indigo with bromine, a compound which can be prepared synthetically with comparative ease. The costliness of this natural dye was almost proverbial, and the reason for this is not far to seek; for the colouring matter obtained by the German chemist from the glands of 12,000 shell-fish, amounted to only about 23 grains, and the estimated cost of the dye was nearly £60 an ounce.

Synthetic Drugs.

The sixteenth and seventeenth centuries are regarded as marking a distinct era in chemistry, inaugurated by Paracelsus. During that period chemistry was looked upon as the handmaid of medicine, and the study of the action of substances on the human organism and the preparation of drugs, were held to be the true functions of the chemist. That was the period of what was called iatro-chemistry.

While the modern chemist would resent the restriction of his functions within such narrow limits, the services which chemistry has, in modern times, rendered to medicine are greater beyond comparison than all the iatro-chemists were ever able to perform. Not only have "Nature's remedies," the juices and extracts of plants, the valuable alkaloids like quinine and morphia, been exhaustively studied and the methods of their extraction improved, but they have been supplemented, in some cases even displaced, by a large array of new drugs and medicinal preparations which owe their origin to the genius and painstaking labours of chemists. The herbalist, in fact, has given place to the scientific chemist, and the manufacture of synthetic drugs, anæsthetics, hypnotics, antipyretics, and drugs for the treatment of special diseases, has developed, in the past thirty years, into an industry of great importance.

The earliest of these synthetic products dates from 1832, when Liebig prepared the anæsthetic chloroform, by the action of bleaching powder on alcohol.[1] Who will dare

[1] Chloroform is now prepared from acetone, a product of the distillation of wood.

to compute the sum of misery and suffering from which this one discovery has freed mankind, or place a money value on the service it has rendered? But the discovery of chloroform has been followed by the discovery of other anæsthetics; general anæsthetics like ether and ethyl chloride (also, like chloroform, produced from alcohol); and local anæsthetics like novocaine (a derivative of coal-tar benzene), used as a substitute for the vegetable alkaloid cocaine.

Side by side with chloroform we may place the closely related compound, iodoform, a yellow crystalline compound largely used as an antiseptic.

Following closely on the discovery of chloroform came the discovery of chloral, the first hypnotic to be produced commercially. But the dangers attending the use of chloral led to the search for and discovery of other hypnotics which are free from the bad qualities of chloral; and at the present day quite a number of synthetic hypnotics are known, of which perhaps the most familiar are veronal, and the inter-related compounds, sulphonal, trional, and tetronal.

If the introduction of the anæsthetic chloroform marked a new era in surgery, a similar claim may perhaps also be made in connection with the substance adrenaline, the active principle of the supra-renal glands. This substance when injected subcutaneously even in excessively minute amount, produces so violent a contraction of the arteries that the blood is driven away from the injected tissues and "bloodless" surgery becomes a possibility.

Adrenaline was isolated for the first time in 1901, from the supra-renal glands of sheep and oxen, close on

1000 lbs. of tissue (the glands from 20,000 oxen) being required to yield 1 lb. of adrenaline. It was not long, however, before the nature of the substance had been determined, and a process for preparing it synthetically on an industrial scale had been devised. It is now placed on the market under the name *suprarenine*.

The compound adrenaline formed in the glands of animals is optically active and rotates the plane of polarised light to the left. It will, however, be understood from the previous chapter that the synthetic product is inactive and a compound of the two optically active forms. This racemic form, as it is called, is only half as active physiologically as the naturally occurring lævo-rotatory form, and it is therefore important to resolve the synthetic compound into its two optically active forms and to isolate the lævo-form. This can be done with the help of dextro-tartaric acid.

The difference in the behaviour of an optically active substance towards the asymmetric living tissues was emphasised in the previous chapter, and an excellent illustration of this property is afforded by adrenaline; for it is found that the physiological action (the increase of the blood pressure) is twelve to fifteen times greater in the case of the naturally occurring lævo-adrenaline than in the case of the synthetic dextro-adrenaline and about twice as great as in the case of the inactive racemic form.

The great development which has taken place in recent times in the industrial production of synthetic drugs is due mainly to the discovery in 1887 of antifebrin, the first of a series of synthetic antipyretics which have entered into competition with the natural alkaloid quinine. Strangely

enough, the discovery of the antipyretic properties of antifebrin, a compound derived from acetic acid and aniline, and known in chemistry as acetanilide, was due to a mistake on the part of a laboratory boy who supplied this substance in mistake for naphthalene. During a pharmacological investigation of the substance, its strongly antifebrile action was detected, and from a chemical analysis, it was learned what the substance really was. The success of this first synthetic antipyretic soon led to the preparation and systematic study of the physiological action of a large number of other substances, but although hundreds, indeed thousands, of these have been found to have a certain medicinal value, only a few have, by their special properties or effectiveness, obtained a place in actual practice. Among synthetic drugs, however, there exists a ceaseless competition, and antifebrin has been largely superseded by newer and better drugs. Antifebrin, as we have seen, is derived from aniline, and is liable to undergo decomposition in the body, giving rise again to aniline which exerts a toxic action; and the continued use of the drug is therefore dangerous. By slightly modifying the composition of antifebrin, however, another compound, the well-known phenacetin, is obtained, a substance which possesses the valuable antipyretic properties of antifebrin, but is much less toxic.

One other synthetic drug of which special mention may be made is the anti-rheumatic, aspirin, a derivative of salicylic acid, which is itself a therapeutic agent of value, and is prepared from the coal-tar product, phenol or carbolic acid. Owing, however, to the large amounts of phenol used in different departments of synthetic

chemistry, the amount obtained from coal tar is quite insufficient to supply the demand, so that phenol itself is now largely manufactured from coal-tar benzene.

Synthetic Perfumes.

If the synthesis of colouring matters and of drugs constitutes an achievement of the greatest importance, the significance of which is all too little realised, scarcely less notable are the successes of the chemist in the synthesis of those natural spices and perfumes, which have been valued by man from the earliest days. For thousands of years the volatile substances to which the different flowers and plants owe their odours have been prepared by distillation or by extraction by means of solvents. But in the past thirty or forty years the secrets of nature have been largely unravelled, and the chemical laboratory has become odorous as a garden and filled with the perfumes of violet and rose, heliotrope, lilac, hyacinth, and orange blossom; and from the stills of the chemist there also flow liquids whose flavours imitate those of the apple, pear, pineapple, and other fruits, and which, in consequence, find application as artificial fruit essences. Although in a number of cases these perfumes and flavouring essences merely imitate the products of nature, in other cases the chemist has succeeded in preparing the identical substances to which the flavour of the natural fruit or the perfume of the growing flower is due.

One of the first of these natural substances to be prepared by the chemist was the substance coumarin, the odoriferous principle of the sweet woodruff (*Asperula*

odorata), a fragrant substance used in the preparation of the perfumes known as Jockey Club and New-mown Hay. This synthetic preparation of a natural odoriferous principle was speedily followed by the preparation of the flavouring material, vanillin, the active principle occurring in the vanilla bean. This substance is now manufactured from toluene, as raw material, and is of great commercial importance. To these earliest synthetic products numerous others have since been added, so that the main odoriferous principles of oil of wintergreen (*methyl salicylate*), oil of bitter almonds (*benzaldehyde*), hawthorn blossom (*anisic aldehyde*), lily of the valley (*terpineol*), ambergris (*ambrein*), and others, can now be prepared artificially. In the case of other synthetic compounds we have substances which, while not identical with the natural perfumes, closely resemble them, and are employed in large quantities either as substitutes for the natural perfumes or for blending with them. Of these the most important are ionone, or imitation violet, imitation musk, and imitation oil of bitter almonds, or "oil of mirbane" (*nitro-benzene*).

The synthetic production of sweet-smelling substances, often at only a fraction of the cost of the natural product, has led to a great extension in the use of such substances, more especially for the perfuming of soaps, creams, and other toilet materials.

We have already seen how the synthetic production of the colouring matters alizarin and indigo have produced vast economic changes by the more or less complete supersession of the natural by the synthetic dyes. In the commercial production of camphor we have another

illustration of the successful synthesis of an important natural product, without, however, the same disastrous consequences to the latter.

Camphor, one of the most familiar of substances, has been produced for many centuries in Japan, Borneo, Formosa, and other regions of the Far East. It is found chiefly in the leaves of a species of the laurel tree, the *Laurus camphora*, from which it is obtained by distilling the leaves or other parts of the tree, in a current of steam. The camphor, being volatile, passes over with the steam and can be condensed in cooled vessels.

Camphor has for long been a highly valued substance on account of its therapeutic, disinfecting, and other properties, but the demand for the compound has been very greatly increased in the past forty years owing to its employment in the manufacture of celluloid or xylonite, and of explosives. Japan had, therefore, a valuable source of revenue in her practical monopoly of the production of camphor through her possession of the plantations of the camphor-tree in Formosa, the extent of which, in the years following the Russo-Japanese War, she very greatly increased; and the monopoly she possessed she sought to exploit to its utmost.

But the substance had long attracted the attention of chemists, and in spite of the difficulty of the problem, its molecular constitution was at length unravelled and the compound prepared synthetically in 1903. Two years later, synthetic camphor, identical in all respects with the substance produced in the camphor-tree, was placed on the market in competition with the natural product.

But the Japanese camphor plantations have hitherto

escaped the fate which befell the plantations of madder, and, so far as can be foreseen, they are not likely to suffer great disaster. The reason for this, however, lies outside the control of the chemist, and is to be found in the scarcity and cost of the raw material used in the manufacture. The source of the raw material is oil of turpentine, an essential oil which is produced in trees belonging to the different species of pine, and which is not only restricted in quantity, but is also subject to increase in price. The synthetic camphor, therefore, has not been able to displace the natural, but it has prevented an excessive rise in the price of the compound.

And now we must conclude. Giving a backward look, we see how out of the mysticism and obscurantism of the earlier alchemistic period there has grown the science of chemistry, which offers to the mind a clear and well-ordered account of the constitution of matter and of the laws of chemical combination. We have seen also, how, during the past hundred years, much has been added not only to our philosophic conceptions regarding the universe of matter, but also to the great array of substances which, in various ways, have proved of benefit to mankind. But great as have been the services rendered by chemistry hitherto, its power to contribute to man's comfort and well-being and to the general advancement of civilisation and of culture, is not yet exhausted; nay, rather, the achievements of the past are but an earnest, we may confidently believe, of what will still be accomplished in the future.

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